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CONTENTS

A symposium on Chemical Kinetics was held on the occasion of the Annual Session of the National Academy of Sciences, India in the Physics Lecture Theatre, Allahabad University. Professor A. C. Chatterji, D.Sc., Dr. Ing., Head of the Department of Chemistry and Dean of the Faculty of Science, Lucknow University, was in the Chair.

Professor S. Ghosh, D.Sc., F.R.I.C., F.N.I., Head of the Department of Chemistry, University of Allahabad, opened the symposium. The speaker emphasised the importance of free radicals in determining the mechanism of Chemical Reactions. He referred to the work on Chemical Reactions being pursued in the Chemical Laboratories of the University of Allahabad. He made a special mention of the Eder's Reaction induced in dark by inductors and pointed out how the reaction can suitably be explained by the production of free radicals either in sun light or in dark by inductors. The speaker also mentioned the work done by him and his collaborators to modify the Abel-Weiss Mechanism of Eder's Reaction.

The following papers were then presented to the Symposium :

(1) A. K. Sinha, A. K. Dey and S. Ghosh (Allahabad): Studies in the reduction of Mercuric Chloride by Oxalate ion in presence of Hydrogen Peroxide.

(2) N. R. Subbaratnam and A. K. Bhattacharya (Sagar): Light Absorption and Chemical Reactions.

(3) S. R. Palit (Calcutta): The General Theory underlying the determination of the Kinetic Constants of Chain Transfer during Polymerisation.

(4) M. P. Singh and S. Ghosh (Allahabad): Study of the reduction of Bivalent Copper by Glucose in presence of Citrate.

(5) M. P. Singh and S. Ghosh (Allahabad):   Kinetics of reduction of Fehling's Solution by Glucose.

(6) A. C. Chatterji and Vareky Antony (Lucknow):   Mechanism of Chromic Acid Oxidations.

(7) U. S. Nandi and S. R. Palit (Calcutta):   Kinetics of the Oxidation of Amine by Hydrogen Peroxide.

(8) S. P. Srivastava and S. Ghosh (Allahabad):   Studies in the Kinetics of the reaction between Hydrogen Peroxide and Potassium Persulphate.

(9) N. R. Subbaratnam and A. K. Bhattacharya (Sagar):   Ultraviolet absorption study of the reaction between Sodium Formate and Iodine.

(10) S. R. Gupta and S. Ghosh (Allahabad):   Catalytic activity of Hydrated Ferric Oxide towards the decomposition of Hydrogen Peroxide.

(11) S. L. Bafna (Poona):   Catalysis by Organic ion exchange Resins.

(12) P. B. Mathur (Allahabad):   The Mechanism of Molecular Activation and the Spectroscopic method for the determination of the velocity constants of Thermal and Photochemical Reactions.

Each paper was followed by a discussion. Among those who participated in the discussions, besides the authors, were Prof. A. C. Chatterji (Lucknow), Dr. Satya Prakash (Allahabad), Dr. K. S. G. Doss (Kanpur), Dr. Bal Krishna (Allahabad) and Dr. R. C. Mehrotra (Allahabad).

The President, Professor A. C. Chatterji, made brief presidential remarks and he emphasised the importance of the study of Chemical Kinetics and pleaded for an attempt to the correct prediction of the mechanism of chemical changes from theoretical considerations. The meeting then closed with a vote of thanks to the Chair.

STUDIES IN THE REDUCTION OF MERCURIC CHLORIDE BY OXALATE ION IN PRESENCE OF HYDROGEN PEROXIDE

Part I. Influence of tripositive iron on the reaction

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ABSTRACT

The reduction of mercuric chloride by potassium oxalate, induced by hydrogen peroxide in the presence of tripositive iron, has been studied in dark. The reaction has been found to be zero-molecular with respect to mercuric ion and unimolecular with respect to oxalate. It has been concluded that $C_2O_4^-$ and OH^- radicals are produced in the system, which are responsible for the reduction of mercuric ion to the mercurous state, by a chain mechanism.

The reaction between mercuric chloride and potassium oxalate, in the presence of oxidising agents like potassium permanganate, potassium persulphate, manganese, dioxide etc., was first observed by Dhar, who suggested the reaction to be an induced one, in dark. It was further noted by Dhar that hydrogen peroxide is able scarcely to promote the reduction of mercuric ion in dark. We have now observed that hydrogen peroxide is able to effect a slight precipitation of calomel in the reaction between mercuric chloride and a soluble oxalate only on boiling and when present in an appreciable concentration. A significant observation has been made by us that heavy metallic ions like tripositive iron, bipositive copper and iron, etc. are able to initiate the reaction between mercuric chloride and potassium oxalate, in presence of low concentrations of hydrogen peroxide even at temperatures below the boiling point. This paper records some of our observations on this work, using tripositive iron compounds in presence of hydrogen peroxide.

EXPERIMENTAL

The chemicals used were all of reagent grade. A Jena bottle coated on the outside with black japan and wrapped with a thick black opaque linen was used as the reaction vessel. In the reaction bottle definite volumes of mercuric chloride and potassium oxalate standard solutions mixed together were taken. This mixture and standard solutions of hydrogen peroxide and ferric salt were kept

separately in a thermostat maintaining constant temperature. The reaction was started by running in required quantities of hydrogen peroxide and ferric salt to the reaction mixture. At suitable intervals of time, 10 c.c. of the reaction mixture was withdrawn and added immediately to 10 c.c. of a solution of potassium iodide of known concentration, standardised previously against a standard mercuric chloride solution. The unreacted potassium iodide was titrated back against the standard mercuric chloride solution, by the method described by Kolthoff and Stenger.[2] The method had already been tested for its accuracy, by several blank determinations at several dilutions. The difference between the original titre value against 10 c.c. of potassium iodide solution and the volume of mercuric chloride required to titrate back the unused potassium iodide in the mixture, gives the unreacted mercuric chloride left in the volume of the reaction mixture pipetted out.

It was found that concentrations of 0·001015M and 0·002030M of hydrogen peroxide in the absence of ferric salts when added to the reaction mixture failed to precipitate any calomel even on boiling. Also, 0·00132M and 0·00264M ferric chloride or 0·001M and 0·002M potassium trioxalato ferriate have no effect on the reaction mixture in the absence of hydrogen peroxide.

The following tables show the effect of ferric chloride when added to the reaction mixture in presence of hydrogen peroxide :—

Table 1

Temperature 60°

$HgCl_2$	0·015M
$K_2C_2O_4{}^{--}$	0·100M
H_2O_2	0·001015M
Fe^{+++}	0·00132M

Time in minutes	Volume of unreacted 0·05M $HgCl_2$ in 10 c.c. of the reaction mixture (c.c.)	k_0 (zero order)
1	3·00	—
15	2·92	0·00571
30	2·84	0·00552
45	2·70	0·00682
60	2·60	0·00678
75	2·50	0·00676
105	2·40	0·00577
135	2·40	—

Table II

Temperature 60°

$HgCl_2$	0·015M
$K_2C_2O_4$	0·100M
H_2O_2	0·001015M
Fe^{+++}	0·00264M

Time in minutes	Volume of unreacted 0·05M $HgCl_2$ in 10 c.c. of the reaction mixture (c.c.)	k_o (zero order)
1	3·00	—
15	2·94	0·00429
30	2·88	0·00414
45	2·82	0·00410
60	2·75	0·00428
75	2·68	0·00432
105	2·55	0·00433

Reaction incomplete.

The results presented in Tables I and II, show that the reaction proceeds zeromolecularly with respect to mercuric chloride. Also it may be seen that the reaction does not proceed beyond 20%, presumably because the acidity of ferric chloride increases with time at this temperature due to hydrolysis. It is well known that H^+ and Cl^- ions have anticatalytic effect on this reaction.

Hence it was thought necessary to employ some other compound of tripositive iron, which may not yield acid as a result of hydrolysis. This was achieved by using potassium trioxalato-ferriate as the source of tripositive iron. The complex was prepared by the method described by Booth and others,[3] and the composition of the complex was checked by chemical analysis. Tables III and IV show the results when the reaction proceeds in the presence of hydrogen peroxide and potassium trioxalatoferriate.

Table III

Temperature 70°

$HgCl_2$	0·015M
$C_2O_4^{--}$	0·100M
H_2O_2	0·001015M
Fe^{+++}	0·001M

Time in minutes	Volume of unreacted 0·05M HgCl$_2$ in 10 c.c. of the reaction mixture (c.c.)	k_0 (zero order)
1	3·00	—
30	2·84	0·005519
60	2·68	0·005333
90	2·50	0·006000
120	2·32	0·006000
150	2·13	0·006333
180	2·00	0·004333
210	1·90	0·003333
3000	1·90	—
		Mean=0·006111

Table IV

Temperature 70°

HgCl$_2$	0·015M
C$_2$O$_4^{--}$	0·050M
H$_2$O$_2$	0·001015M
Fe^{+++}	0·01M

Time in minutes	Volume of unreacted 0·05M HgCl$_2$ in 10 c.c. of the reaction mixture (c.c.)	k_0 (zero order)
1	3·00	—
30	2·94	0·002069
60	2·88	0·002000
90	2·80	0·002666
120	2.73	0·002333
150	2·67	0·002000
180	2·60	0·002333
240	2·45	0·002500
300	2·45	—
		Mean= 0·002253

The above tables show that the reaction in the presence of potassim trioxa-latoferriate proceeds farther than with ferric chloride. The order of the reaction with respect to C$_2$O$_4^{--}$ has been calculated with the mean velocity constants of tables III and IV, by the formula :

$$n=\frac{\log k_1-\log k_2}{\log^2}$$

the symbols having their usual significance, and the value of n approximates unity.

So the total order of the reaction is unity, since the reaction is zero order with respect to mercuric ion, and unimolecular with respect to oxalate. It is interesting to note that the reaction has a period of induction.

Incidentally, it was thought necessary to study the effect of varying concentrations of hydrogen peroxide and the ferric ion on the reaction, and the results obtained are tabulated below :

Table V

Temperature 70°

$HgCl_2$	0·015M
$C_2O_4^{--}$	0·100M
H_2O_2	0·001015M
Fe^{+++}	0·002M

Time in minutes	Volume of unreacted 0·05M $HgCl_2$ in 10 c.c. of the reaction mixture (c.c.)	k_o (zero order)
1	2·99	—
20	2·84	0·007600
45	2·65	0·007666
75	2·42	0·007666
105	2·19	0·007666
165	1·73	0·007666
225	1·43	0·005000
285	1·16	0·004500

For the completion of the reaction as ascertained by boiling 10 c.c. of this reaction mixture, the titre value comes out to be 1·00 c.c. In this case the reaction proceeds to the extent of 66% in terms of the reduction of mercuric chloride.

Table VI

Temperature 70°

$HgCl_2$	0·115M
$C_2O_4^{--}$	0·100M
H_2O_2	0·00203M
Fe^{+++}	0·001M

Time in minutes	Volume of unreacted 0·05M HgCl₂ in 10 c.c. of the reaction mixture (c.c.)	k_a (zero order)
1	3·00	—
30	2·84	0·005519
60	2·65	0·006333
60	2·46	0·006333
120	2·26	0·006666
180	1·94	0·005333
240	1·64	0·005000

In this case the titre value obtained by boiling 10 c.c of the reaction mixture is 1·40 c.c. The reaction goes to the extent of 46·6 , in terms of the reduction of mercuric chloride.

On comparing the above tables with Tables III and IV, we find that the reaction becomes faster with the increase in the concentration of Fe^{+++} and H_2O_2. The percentage of reduction of mercuric chloride also is enhanced in tables V and VI. It may further be noted that the increase in the reaction velocity is more pronounced with the increase in the concentration of ferric ion.

The complex trioxalato ferriate has been found to have no effect on the reaction in the absence of hydrogen peroxide in dark, but as this complex is known to undergo photochemical decomposition in sunlight (vide Dhar[1]) it was thought to be of interest to study the effect of the photolysed complex on the reaction in dark in the absence of hydrogen peroxide. The solution of the complex was exposed to sunlight for different periods of time and immediately added to the reaction mixture in dark, and the progress of the reduction of mercuric chloride by potassium oxalate studied as before. The results are shown in tables VII and VIII. It should be mentioned that the activity of the exposed complex lasts for several hours, as has been studied by some experiments not recorded in this paper.

Table VII

Temperature 25°

HgCl₂	0·02084M
K₂C₂O₄	0·0833M
Complex (exposed to sunlight for 10 minutes)	0·00166M

Time in minutes	Volume of unreacted 0·05M HgCl$_2$ in 5 c.c. of the reaction mixture (c.c.)	k_o (zero order)
0	2·10	—
2	1·90	0·1000
17	1·66	0·0160
32	1·56	0·0066
47	1·50	0·0040
62	1·47	0·0020
77	1·47	—

Table VIII

Temperature 25°

HgCl$_2$	0·02084M
K$_2$C$_2$O$_4$	0·0833M
Complex (Exposed to sunlight for 20 minutes)	0·00166M

Time in minutes	Volume of unreacted 0·05M HgCl$_2$ in 5 c.c. of the reaction mixture (c.c.)	k_o (zero order)
0	2·10	—
2	2·00	0·0500
17	1·88	0·0080
32	1·82	0·0040
47	1·77	0·0033
62	1·70	0·0047
77	1·63	0·0047
107	1·54	0·00300
137	1·47	0·0023

The observations recorded in tables VII and VIII show that the reaction with the photolysed complex is too fast in the beginning and the velocity falls off to reach a constant value, showing the zeromolecular nature of the reaction with respect to mercuric chloride. Further, these tables indicate that there is an optimum time of exposure of the complex to sunlight, in order to produce the maximum effect.

From the observations recorded in this paper, we conclude that potassium trioxalato ferriate exposed to sunlight or mixed with hydrogen peroxide produces

$C_2O_4^-$ ions, the existence of which was postulated by Abel[5] and further elucidated by Weiss,[6,9] and Uri[7,8]. This active product $C_2O_4^-$ and the free redical OH are able to initiate a chain reaction, resulting in the reduction of mercuric chloride to calomel.

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THE GENERAL THEORY UNDERLYING THE DETERMINATION OF THE KINETIC CONSTANTS OF CHAIN TRANSFER DURING POLYMERIZATION

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[Communicated by Professor S. Ghosh, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc.]

The rate at which a growing polymer radical attacks the surrounding solvent is generally determined by Mayo's method[1,2,3] of plotting $1/\overline{P}_n$ against S/M where $\overline{P}_n$ is the average degree of polymerization and S/M is the ratio solvent : monomer ; the slope of the above line gives the ratio k_s/k_p where k_s is the rate of chain transfer and k_p is the rate of propagation of the chain. The method, however, requires careful scrutiny and assessment as regards its theoretical basis and the present paper is an attempt in that direction.

Derivation of the General Equation :—If there is present in a polymerizing system any speices, X, which may be a molecule or a free radical capable of reacting with a growing radical, $C^\star$ either by chain transfer or by coupling with a rate k_x, the rate of cessation of chain is equal to $k_x \times C^\star$. This is true for all such speices present.

$$\text{Rate of cessation of chain} = k_x X C^\star \qquad \dots\dots\dots\dots(1)$$

But, Rate of propagation of chain,

$$R_p = -dm/dt = k_p C^\star M \qquad \dots\dots\dots\dots(2)$$

where $C^\star$ is the total concentration of growing radicals at any instant, M is the monomer concentration, and R_p stands for the rate of monomer consumption.

Hence if the number average degree of polymerization is $\overline{P}_n$ we have

$$\frac{1}{P_n} = \frac{\text{Rate of cessation of chain}}{\text{Rate of propagation of chain}} = \frac{\Sigma k_x X C^\star}{R_p} = \frac{\Sigma k_x X C^\star}{k_p C^\star M}$$

$$\therefore \quad \frac{1}{P_n} = \Sigma \frac{k_x}{k_p} \cdot \frac{X}{M} \qquad \dots\dots\dots\dots(3)$$

$$\therefore \quad \frac{1}{P_n} = \Sigma C_x \cdot \frac{X}{M} \qquad \dots\dots\dots\dots(4)$$

where C_x is the ratio of the two constants, k_x/k_p. In the rest of the paper we shall write $\overline{P}$ or $\overline{P}_n$. This equation (4) is our fundamental equation for D. P.

Applying equation (4) to the case of a polymerizing system composed of a monomer, M, a solvent, S and an initiator (catalyst), I, we get,

$$\frac{1}{P} = C_m \frac{M}{M} + C_s \frac{S}{M} + C_i \frac{I}{M} + C_c \star \frac{C\star}{M} \qquad \dots\dots\dots\dots(5)$$

where $C_c\star$ by our definition of C_x is of course k_t/k_p, k_t being the rate of termination by interaction between two growing radicals.

Now, combining equations (2) and (5) to eliminate $C\star$, we have

$$\frac{1}{P} = C_m + C_s \frac{S}{M} + C_i \frac{I}{M} + \frac{k_t}{k_p^2} \cdot \frac{1}{M^2} \cdot R_p \qquad \dots\dots\dots\dots(6)$$

writing δ for $k^{\frac{1}{2}}_t/k_p$, this equation becomes,

$$\frac{1}{P} = C_m + C_s \frac{S}{M} + C_i \frac{I}{M} + \frac{\delta^2}{M^2} \cdot R_p \qquad \dots\dots\dots\dots(7)$$

which is our general equation. For S=O, or for I=O (no catalyst this equation transforms into equation (8) and (9) respectively).

$$\frac{1}{P} = C_m + C_i \frac{I}{M} + \frac{\delta^2}{M^2} \cdot R_p \qquad \dots\dots\dots\dots(8)$$

$$\frac{1}{P} = C_m + C_s \frac{S}{M} + \frac{\delta^2}{M^2} \cdot R_p \qquad \dots\dots\dots\dots(9)$$

Equations (7) and (8) or their equivalent forms have, however, been already derived by a different method from general kinetic considerations by Baysal and Tobolsky[4] and Johnson and Tobolsky,[5] and their experimental implications have been investigated by Palit, Nandi and Saha.[6]

The Current Method in the Light of our General Equation:—The current method which is due to an equation deduced by Mayo for uncatalysed polymerization (*i.e.*, I=0), makes the doubtful assumption which in our terminology is equivalent to assuming (at I=0)

$$\frac{1}{P_o} = \left(\frac{1}{P} \right)_{s=0} = C_m + C_c \star \frac{C\star}{M} \qquad \dots\dots\dots\dots(10)$$

which is easily obtained by putting I=0 and S=0 in equation (5). By combining equation (10) with equation (5) we get Mayo's equation

$$\frac{1}{P} = \frac{1}{P_o} + C_s \frac{S}{M} \qquad \dots\dots\dots\dots(11)$$

This first step though apparently satisfactory has a deep lying fallacy. According to this equation $C\star/M$ should be a constant. This is not generally true

either theoretically or experimentally though in the case of styrene, which has been most investigated, equation (10) is very near to truth. The experimental fallacy is apparent in the case of methyl methacrylate where it has been found[2] that though $1/\bar{P}$ versus S/M plot is linear, the intercept is widely divergent from $1/\bar{P}_0$ for bulk polymerization. A more disturbing discrepancy is that the intercept is even different for different solvents in many cases.

Theoretically, the root cause of this fallacy lies in the fact that though k_p and k_t being free radical reactions hardly change by a change in solvent, k_i which is a rate constant of the usual type is liable to vary widely from solvent to solvent not only confirmity with the well-known but still unexplained phenomenon of 'solvent effect' on reaction kinetics but also due to varying 'cage effect' with varying dilution of a monomer. This change of k_i with varying S/M makes Mayo's expression for $1/\bar{P}_0$ (equation 10) of restricted validity as $C*/M$ would not yield a constant value under such conditions in different solvents at same S/M.

The validity and limitation of Mayo's equation are brought home by writing equation (9) in the following form:

$$\left[\frac{1}{\bar{P}} - \frac{\delta^2}{M^2} \cdot R_p\right] = C_m + C_s \frac{S}{M} \qquad \ldots\ldots\ldots\ldots(12)$$

It is easily seen that if R_p is proportional to M^2 the second term on the left of the above equation is constant and so Mayo's method would be valid, i.e., the slope of $1/\bar{P}$ versus S/M would be equal to C_s. In thermal polymerization in many cases specially in the case of styrene R_p is proportional of M^2 and so Mayo's method gives correct results.

In cases where R_p is not proportional to M^2, Mayo's method will give incorrect results, and all the existing data on chain transfer which have been obtained by the use of Mayo's equation are subject to the above uncertainity. Fortunately, however, in styrene and in a few more cases R_p is very nearly proportional to M^2 in thermal polymerization in many solvents and so Mayo's equation gives correct results with these solvents. But still unless the above proportionality is experimentally demonstrated, the data cannot be unconditionally accepted.

It is hence concluded that Mayo's equation should be replaced by our equation (12) and for a more generalised treatment by our equation (6), and methods based on the latter equations should be used for chain transfer determinations.

It is pertinent, however, to point out an interesting consequence of equation (12). Even if R_p is not proportional to M^2 over the whole range of

solvent : monomer, it can be easily seen that Mayo's method is still valid for the determination of C_s, provided we choose to work on a range of S/M only over which R_p is proportional to M^2. In such cases, however, the intercept on the $1/\bar{P}$ axis will not be equal to $(1/\bar{P}_0)_{obs}$ where P_0 is the D. P. for observed experimental bulk polymerization. Two simple cases can be easily described. The actual rate of bulk polymerization (bulk R_p) may be either higher or lower than that obtained by extrapolating to bulk concentration the R_p versus M^2 line obtained over the valid experimental range of S/M. In the formal case the observed reciprocal of D. P., i.e., $(1/\bar{P}_0)_{obs}$ will be greater than the extrapolated value, i.e., $(1/\bar{P}_0)_{extrap}$. and the reverse would be true in the latter case. With methyl methacrylate we have observed[2] that for many solvents $(1/\bar{P}_0)_{extrap}$ is greater than $(1/\bar{P}_0)_{obs}$ for which we failed to offer a suitable explanation at that time. From the present analysis it is now expected that for such anomalous solvent-methyl methacrylate systems, R_p versus M^2 curve would be of the second type, i.e., from a linear curve it would become concave towards the M^2 axis as we approach bulk polymerization. We can express it alternatively by saying that log R_p versus log M curve should have a slope less than two near bulk thermal polymerization for the anomalous solvent. This point is now receiving close experimental attention is our laboratory.

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KINETICS OF REDUCTION OF FEHLING'S SOLUTION BY GLUCOSE

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ABSTRACT

In this paper the present authors have determined the order with respect to copper sulphate in the reduction of Fehling's solution by glucose. They have found that the reaction is of zero order with respect to copper sulphate and has a little induction period. The amount of tartrate equivalent to the concentration of copper sulphate to form the complex is essential for the reduction of copper but any excess of the tartrate does not appreciably affect the reaction velocity. The minimum amount of alkali required for the reaction is equivalent to the amount of copper sulphate and the increase in concentration of the alkali beyond this amount increases the reaction velocity and also the induction period is diminished.

A large amount of work has been done on the reduction of Fehling's solution by different reducing agents but little work seems to have been done in determining the mechanism of the kinetics of this reduction. Urech[1] has studied the rate of reduction of Fehling's solution with a view to determine the composition of invert milk sugar. Several authors have investigated the colloidal and photochemical nature of Fehling's solution. In this paper the present authors have attempted to elucidate the order of the reaction with respect to copper sulphate in Fehling's solution by taking glucose as a reducing agent. We have also investigated the effect of concentration of tartrate and sodium hydroxide on the reaction velocity by studying the reduction of copper sulphate containing various proportions of alkali and tartrate. All the kinetics have been studied at 30°C in dark.

EXPERIMENTAL

Several Pyrex conical flasks (100 ml.) are taken and into each of them 30 c.c. of solution containing copper sulphate, sodium potassium tartrate and sodium hydroxide of known concentrations are taken and kept in dark in a thermostat. 10 ml. of freshly prepared glucose solution maintained at the temperature of thermostat are run into each conical flask and the time at which the solution is run in, is noted in each case. The amount of cuprous oxide precipitated in each conical flask at definite time (time varying from flask to

flask) is estimated by quenching the reaction by pouring out the contents of the reaction bottle into ice cold water. The cuprous oxide is filtered out and washed several times with distilled water till it is free from impurities. This cuprous oxide is oxidised (Clarke[2]) by an excess of pure ferric sulphate solution. The amount of ferrous ion formed is estimated by a standard potassium dichromate solution using N-phenyl anthranalic acid as indicator. The amount of ferrous sulphate formed corresponds to cuprous oxide in each case. It should be noted that each reading of a given table is taken from a different reaction flask.

Tables I and II are typical tables of several experiments showing the general trend of the reaction and the action of alkali in guiding the reaction. The molecular concentration of glucose is $=1.76$ times that of copper sulphate, but as one molecule of glucose require six molecules of copper sulphate (Clarke[2]), the equivalent concentration of glucose is $6 \times 1.76 =$ more than 10 times that of copper sulphate.

A perusal of the tables show that the reaction rate is slow in the beginning and then it becomes almost constant throughout the course of reaction followed. Further tables show that speed is considerably increased by increasing the amount of alkali. The rate constant is zero molecular with respect to copper sulphate.

Table I Temerature 30°C			*Table II* Temerature 30°C		
0.0174M	$CuSO_4$		0.0174M	$CuSO_4$	
0.0234M	Tartrate		0.0234M	Tartrate	
0.0622M	NaOH		0.1244M	NaOH	
0.0306M	Glucose		0.0306M	Glucose	
Time (minutes)	0.05N $K_2Cr_2O_7$ X	X/T	Time (minutes)	0.05N $K_2Cr_2O_7$ X	X/T
30	1.00 ml.	0.0333	20	1.15 ml.	0.0575
50	2.20	0.0440	30	2.20	0.0733
70	3.20	0.0455	40	3.25	0.0812
91	4.15	0.0456	50	4.20	0.0840
110	5.00	0.0454	60	5.05	0.0841
130	5.35	0.0410	70	5.85	0.0835
160	6.05	0.038	80	6.70	0.0837
190	7.50	0.0395	90	8.00	0.0888
220	10.00	0.0454	100	9.50	0.0950
T ∞	13.50	—	T ∞	13.50	—

Effect of Increasing Amount of Sodium Hydroxide on the Reaction Velocity.

It is observed from tables I to V that the reaction velocity increases rapid-ly by increasing the amount of alkali. We see that the induction period gradu-ally diminishes on increasing the amount of alkali. It further shows that increase in velocity constant with increasing alkali concentration approaches a maximum value, which becomes almost constant.

Table III			*Table IV*		
Temperature 30°C			Temperature 30°C		
0·0174M	$CuSO_4$		0·0174M	$CuSO_4$	
0·1543M	NaOH		0·1870M	NaOH	
0·0234M	Tartrate		0·0234M	Tartrate	
0·0306M	Glucose		0·0306M	Glucose	

Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T	Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T
10	0·60 ml.	0·060	10	0·70 ml.	0·070
15	1·05	0·070	15	1·20	0·080
20	1·75	0·087	20	1·85	0·092
25	2·30	0·092	25	2·50	0·100
30	2·70	0·090	30	3·10	0·103
35	3·17	0·090	35	3·60	0·103
40	3·60	0·090	40	4·15	0·103
45	4·10	0·091	50	5·10	0·102
55	5·05	0·091	60	6·00	0·100
T∞	13·50	—	T∞	13·50	—

Table V		
Temperature 30°C		
0·0174M	$CuSO_4$	
0·0234M	Tartrate	
0·02488	NaOH	
0·0306M	Glucose	

Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T	Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T
10	1·00 ml.	0·100	35	4·25 ml.	0·121
15	1·80	0·120	40	4·95	0·121
20	2·50	0·125	50	6·00	0·120
25	3·10	0·124	60	7·40	0·123
30	3·70	0·123	T ∞	13·50	—

Effect of Variation of the Concentration of Tartrate on the Reaction Velocity.

In presence of copper sulphate and sodium hydroxide sodium potassium tartrate forms complex with the immediately precipitated cupric hydroxide, thus it keeps copper in solution. This complex has been studied by Pickering[3] and in great detail by Bobtelsky and Jordon[4] in neutral and alkaline medium. The latter authors have shown that one molecule of copper sulphate requires one molecule of tartrate. We have also taken tartrate nearly equivalent to copper sulphate.

It is further marked from Tables VI, VII, VIII and IX at two different concentrations of alkali, that the reaction velocity is independent of the concentration of tartrate, but a minimum amount of tartrate (equivalent to copper sulphate) is essential for the reduction of copper.

Table VI

Temperature 30°C

0·0174M	$CuSO_4$
0·0622M	NaOH
0·0306M	Glucose
0·0468M	Tartrate

Table VII

Temperature 30°C

0·0174M	$CuSO_4$
0·0622M	NaOH
0·0306M	Glucose
0·0936M	Tartrate

Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T	Time (minutes)	0·05N $K_2Cr_2O_7$ X	X/T
30	1·10	0·0333	30	0·90	0·0300
50	1·80	0·0360	50	1·80	0·0660
70	2·40	0·0343	70	0·60	0·0371
90	3·20	0·0353	90	3·40	0·0378
110	4·05	0·0368	110	4·95	0·0380
150	5·40	0·0360	150	5·75	0·0383
170	6·50	0·0383	180	7·00	0·0989
190	7·60	0·0400	210	8·60	0·0409
T ∞	13·50	—	T ∞	13·50	—

Table VIII				Table IX		

Temperature 30°C   Temperature 30°C

0·0174M	CuSO$_4$			0·0174M	CuSO$_4$	
0·1244M	NaOH			0·1244M	NaOH	
0·0306M	Glucose			0·0306M	Glucose	
0·0468M	Tartrate			0·0936M	Tartrate	

Times (minutes)	0·05N K$_2$Cr$_2$O$_7$ X	X/T	Time (minutes)	0·05N K$_2$Cr$_2$O$_7$ X	X/T
20	1·20	0·0600	20	1·35	0·0675
30	2·30	0·0766	30	2·45	0·0818
41	3·00	0·0804	40	3·35	0·0833
50	3·95	0·0790	50	4·30	0·0860
60	4·90	0·0816	60	5·30	0·0883
70	5·70	0·0814	70	6·15	0·0886
80	6·80	0·0850	80	7·10	0·0886
90	7·85	0·0870	90	8·75	0·0972
100	10·00	0·1000	100	11·20	0·1120
T∞	13·50	—	T∞	13·50	—

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MECHANISM OF CHROMIC ACID OXIDATIONS

Part I. Oxidation of sec-Butyl alcohol : by Chromic acid

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INTRODUCTION

Kinetic studies of oxidations by Chromic acid of various organic and inorganic substances have been made by various workers. Chromic acid has been used to oxidise arsenious acid,[1] ferrous iron,[2] formic acid,[3] phosphorous acid,[3] aromatic aldehydes,[4] iodide ion,[5] uranyl ion,[6] and oxalic, lactic and maleic acids.[7,11] Some photochemical studies have been made in which Chromic acid acts as the oxidising agent by Dhar and Bhattacharya[8] and by Bowen.[9] Some studies involving Chromic acid have also been made in the heterogeneous phase.[10] In all these reactions the chromic acid oxidises the organic or inorganic substance in presence of some inorganic acid, the H^+ ions serving as the catalyst. But detailed studies sufficient to assign a complete mechanism are lacking in most of these cases. No attention has been paid to the total ionic strength of the reaction mixture ; the ionic strength affects the activity of the reactants and hence it has to be kept constant throughout the experiments. Again the role of the acid catalyst has not been explained.

Recently the oxidation of iso-Propyl alcohol has been studied by Westheimer and co-workers in presence of perchloric acid as source of H^+ ions and at a constant ionic strength ; a probable mechanism has been given in which intermediate ions of valency between six and three are shown to play an important part. But no other oxidations have been studied in such detail. In this paper the oxidation of sec-Butyl alcohol has been studied with a view to suggest a suitable mechanism which would explain all the experimental facts.

CHEMICALS AND TECHNIQUE

The chromic acid was B. D. H. analar grade and was re-crystallised from water. The chromic acid content was determined iodometrically.

B. D. H. grade sec-Butyl alcohol was kept over potassium hydroxide for 24 hours and distilled; it was then refluxed over calcium metal for six hours and distilled ; the fraction boiling between 99 and 100 degrees was collected. It had a density of 0·7954 gms/cc.

The thermostat was controlled up to $\pm 0.05°C$. The progress of the reaction was followed by pipetting out aliquot portions of the reaction mixture into ice cold water containing potassium iodide and sulphuric acid, and titrating the liberated iodine against standard thiosulphate.

The oxidation was studied in presence of perchloric acid as the source of H^+ ions. The total ionic strength of the reaction mixture was kept constant at $0.4M$, sodium perchlorate being added if necessary. In calculating the total concentration of H^+ ions the equilibrium between acid-chromate and dichromate ions,

$$Cr_2O_7^{--} + H_2O = 2HCrO_4^- \quad\ldots\ldots\ldots\ldots\ldots(i)$$
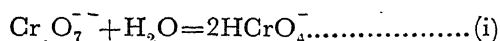
was taken into account. A value of 0.0176 was used for the equilibrium constant of this reaction[13] at $35°C$ and an ionic strength of 0.4.

A series of experiments were made in which the concentrations of alcohol and acid were kept constant and were large compared to that of chromic acid which was varied a hundred fold. The concentrations of alcohol and acid were then varied in turn keeping the other two reactants constant. The results are given in the following tables. The K values given are with respect to chromic acid in all the tables.

Table I. Order with respect to Chromic Acid.

Sec-Butyl alcohol 0.2152 M; $HClO_4$ 0.2993 M.

A. CrO_3 0.001 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0.0	17.8	...
18.6	9.7	3.257
24.8	8.0	3.225
30.9	6.55	3.236
36.7	5.4	3.250

B. CrO_3 0.0025 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0.0	17.35	...
15.1	11.1	2.957
20.8	9.1	3.102
32.5	6.3	3.119
39.1	5.0	3.186

C. CrO_3 0.005 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0.0	19.9	...
15.8	13.2	2.598
21.6	11.15	2.69
28.0	9.25	2.736
35.2	7.7	2.700

D. CrO_3 0.01 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0.0	20.05	...
18.0	13.5	2.198
25.8	11.0	2.327
32.9	9.3	2.335
39.9	7.85	2.352

Table II.   Order with respect to sec-Butyl alcohol.

CrO_3 0·001 M ; $HClO_4$ 0·2993 M.

A.   sec-Butyl alcohol 0·04304 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	25·8	...
17·7	23·0	0·6494
43·1	19·7	0·6257
57·6	18·0	0·6249
68·3	16·85	0·6239

C.   sec-Butyl alcohol 0·1292 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	25·8	...
25·8	15·8	1·900
32·6	13·9	1·898
39·6	12·1	1·913
47·8	10·4	1·902

B.   sec-Butyl alcohol 0·08608 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	25·8	...
26·6	18·2	1·312
39·6	15·5	1·287
49·4	13·55	1·304
61·2	11·8	1·278

D.   sec-Butyl alcohol 0·1722 M.

Time (mts)	Thio (ccs)	$k_1.10^2$.
0·0	25·8	...
15·1	17·5	2·572
23·2	14·6	2·454
31·4	11·7	2·519
47·9	7·65	2·538

Table III.   Order with respect to H⁺ions.

CrO_3 0·001 M ; sec-Butyl alcohol 0·2152 M.

A. $HClO_4$ 0·01158 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	21·0	...
106·0	18·3	0·1297
144·0	18·2	0·09932
233·0	18·0	0·06612
285·0	17·8	0·05781
336·0	17·7	0·05086
458·0	17·3	0·04234

D. $HClO_4$ 0·1498 M.

Time (mts)	Thio (ccs)	$k_1.10^2$.
0·0	30·5	...
10·2	28·1	0·7948
21·7	25·5	0·8391
32·4	22·75	0·9070
42·8	21·0	0·8744
55·2	18·5	0·9046
66·1	17·1	0·8754

B. $HClO_4$ 0·02316 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	21·0	...
106·0	18·3	0·1297
142·0	17·8	0·1164
232·0	17·0	0·0911
284·0	16·8	0·07859
334·0	16·3	0·07587
457·0	16·0	0·05953

E. $HClO_4$ 0·22452 M.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	30·5	...
8·8	25·9	1·858
15·8	22·6	1·897
21·2	20·5	1·874
28·7	17·75	1·886
34·9	16·0	1·849
41·4	14·05	1·881

C. $HClO_4$ 0·03474 M.			F. $HClO_4$ 0·3742 M.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	21·0	...	0·0	30·5	...
106·0	17·75	0·1583	5·0	23·6	5·13
140·0	17·3	0·1385	10·0	18·3	5·10
219·0	16·3	0·1157	15·0	14·6	4·19
278·0	15·4	0·1116	21·0	10·85	4·922
331·0	14·85	0·1047	27·0	3·2	4·867
457·0	14·0	0·0889	...	...	...

Table IV.   Effect of metallic salts on the velocity.

CrO_3 0·001 M ; $HClO_4$ 0·1640 M ; alcohol 0·2152 M.

A.   No metallic salt.

Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	27·5	...	0·0	12·3	...
20·1	21·6	1·201	10·0	11·3	0·8473
30·0	19·0	1·232	20·0	10·3	0·888
40·0	16·8	1.232	30·0	9·4	0·8968
50·1	14·8	1·237	38·0	8·9	0·8519

B. Ceric sulphate			D. Manganese sulphate		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	29·0	...	0·0	29·0	...
16·0	26·1	0·902	12·0	27·0	0·595
24·0	23·6	0·859	20·0	26·0	0·5459
32·1	22·1	0·846	30·0	24·6	0·5489
40·0	21·6	0·736	42·0	21·5	0·7128

Table V.   Temperature Co-efficients of the reaction.

A. CrO_3 0·001 M ; sec-Butyl alcohol 0·2152 M ; $HClO_4$ 0·2200 M.

Temp. 25°C.			Temp. 35°C.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	19·8	...	0·0	20·0	...
8·0	18·35	1·060	14·1	14·8	2·134
23·0	15·15	1·065	20·0	13·0	2·158
38·0	13·2	1·067	26·0	11·4	2·162

B. CrO_3 0·002 M; sec-Butyl alcohol 0·2152 M; $HClO_4$ 0·2200 M.

Temp. 25°C.			Temp. 35°C.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	40·65	...	0·0	39·75	...
18·0	34·25	0·9520	23·0	25·85	1·871
26·0	31·7	0·9558	28·0	23·85	1·824
34·0	29·5	0·9426	34·0	20·95	1·883
42·0	27·3	0·9476	42·0	18·2	1·860

C. CrO_3 0·001 M; sec-Butyl alcohol 0·1291 M; $HClO_4$ 0·2200 M.

Temp. 25°C.			Temp. 35°C.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	21·4	...	0·0	20·6	...
22·0	19·1	0·5171	14·5	17·6	1·086
32·0	18·1	0·5233	22·0	16·2	1·086
42·0	17·25	0·5138	29·0	15·0	1·092
52·0	16·4	0·5120	44·0	12·9	1·063

D. CrO_3 0·001 M; sec-Butyl alcohol 0·2152 M; $HClO_4$ 0·3850 M.

Temp. 25°C.			Temp. 35°C.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	18·3	...	0·0	17·6	...
14·0	12·3	0·840	5·0	13·4	5·454
19·0	11·0	2·680	8·0	11·4	5·430
24·0	9·4	2·777	11·0	9·9	5·220

E. CrO_3 0·001 M; sec-Butyl alcohol 0·2152 M; $HClO_4$ 0·2200 M.

Temp. 15°C.			Temp. 45°C.		
Time (mts)	Thio. (ccs)	$k_1.10^2$.	Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	22·0	...	0·0	19·4	...
10·0	21·0	0·4652	8·0	13·95	4·122
39·0	18·35	0·4647	12·0	12·1	3·935
64·0	16·4	0·4592	20·0	9·05	3·814
68·0	16·15	0·4650	24·0	7·35	4·045

Temp. 55°C.

Time (mts)	Thio. (ccs)	$k_1.10^2$.
0·0	19·15	...
2·0	16·4	7·75
4·0	14·45	7·035
8·0	11·0	6·928
10·0	9·35	7·17
12·0	8·2	7·067

RESULTS AND DISCUSSION

The values of k in Table I show very good constancy. This means that the order of the reaction is one, beyond doubt. The value of the velocity constant increases with decrease in chromic acid concentration. This has been reported by many of the earlier workers; this means that the acid chromate ion $HCrO_4^-$ is the most important ion which takes part in the oxidation. (cf. eqn. 1.)

Table II gives the effect of the variation of alcohol concentration on the velocity constants with respect to chromic acid. From these values the order of the reaction with respect to the alcohol was calculated by the following method.[14] The velocity of the reaction may be represented by an equation of the type,

$$-\frac{dc_1}{dt}=kc_1{}^m\,c_2{}^n\,c_3{}^p.$$

where c_1, c_2, c_3 represent the concentrations of chromic acid, sec-Butyl alcohol and H^+ ions, and k the intrinsic velocity constant. This equation can be written as

$$-\frac{dc_1}{dt}=K_1\,c_1{}^m \quad \text{where,}$$

k_1 is the velocity constant with respect to chromic acid and involves the concentrations of alcohol and acid in a manner expressed by the equation.

$$K_1=kc_2{}^n\,c_{3p}.$$

If in two experiments the initial concentrations of chromic acid and H^+ ions are kept constant while that of the alcohol are varied, viz $c_1{}'$ and $c_2{}''$ and k' and k'' are the velocity constants with respect to chromic acid we get,

$$K_1{}'=k'c_2{}^{n\cdot}\,c_3{}^p \quad \text{and}$$

$$K_2{}''=k''c_2{}''^n\,c_3{}^p.$$

From these we get,

$$n=log\frac{K_1{}'}{K_1{}''}\Big/\;log\frac{c_2{}'}{c_2{}''}$$

Applying this method to the date in Table II the following values for the order are obtained :

From A and B, $n=1\cdot05$
   B and C, $n=0\cdot95$
   C and D, $n=0\cdot98$
   D and E, $n=1\cdot12$

This clearly shows that the order with respect to alcohol is one.

The order of reaction with respect to H^+ ion was calculated by the same method ; thus we get,
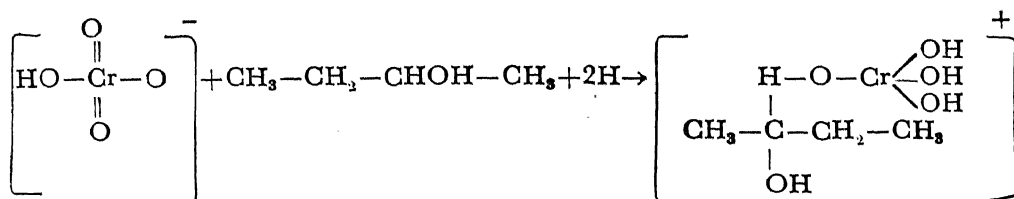
From A and B, $n = 1 \cdot 01$

B and C, $n = 1 \cdot 04$

D and E, $n = 1 \cdot 84$

E and I-A, $n = 1 \cdot 92$

F and I-A, $n = 1 \cdot 85$

These values show that at low concentrations of H^+ ions one H^+ ion takes part in the formation of the activated complex while at high concentrations two H^+ ions take part. The H ions are regenerated since they do not actually take part in the reaction, but only act as catalyst. They only facilitate the formation of a low energy requiring activated complex, which then decomposes to form the product and the H^+ ions. The activated complex may be formulated thus ;

$$\left[\begin{array}{c} O \\ \| \\ HO-Cr-O \\ \| \\ O \end{array} \right]^{-} + CH_3-CH_2-CHOH-CH_3 + 2H \rightarrow \left[\begin{array}{c} H-O-Cr{\overset{OH}{\underset{OH}{\diagdown}}}^{OH} \\ | \\ CH_3-C-CH_2-CH_3 \\ | \\ OH \end{array} \right]^{+}$$

Some experiments were also carried out to determine the effect of light; the effect of light was found to be little. Similarly ethyl methyl ketone was also found to have hardly any effect on the velocity of the reaction. The reaction was studied in the presence of salts of Li, Rb, Cs U, Ti, Zr, Co, Ce, Cu, Cd, Ni, Sb, Al, Mo, Pt, and manganese. It was found that only Mn, Ce, and Cd had some effect on the reaction ; these reduced the velocity of the reaction appreciably. The effect of manganese was remarkable. Even at as low a concentration as $0 \cdot 0001$ M it reduced the velocity to about 60% ; as the reaction proceeded the reaction mixture turned brown and a precipitate of MnO_2 was formed. A similar observation has been made in the case of iso-Propyl alcohol by Westheimer. The sec-Butyl alcohol induces the oxidation of manganese sulphate to manganese dioxide, which is not oxidised by chromic acid in the absence of the alcohol. A detailed examination of this phenomenon has been given in the next section.

Temperature Coefficient and Energy of Activation

From Table V the temperature co-efficient of the reaction, $i.e.$, the ratio $k_5{}^c/k_{.5}{}^o$ was calculated; the energy of activation was calculated using the Arrhenius equation,

$$log_e k = - \frac{E}{RT} + const.$$ which on integration gives,

$$E = \frac{2 \cdot 303 \ log_{10} \frac{k_2}{k_1} RT_1 \ T_2}{T_2 - T_1}$$ where R has the e value 1·987 cals/degree.

The following results are obtained :

Reaction	Temp. Coeff. 25°—35°C	Energy of activation.
A	2·044	13040 cals
B	1·961	12320 „
C	2·094	13520 „
D	2·019	12850 „

The reaction has an average activation energy of 13000 cals between 25°C and 35°C. The following results were obtained for the effect of variation of temperature on the temperature coefficients and energies of activation :

Temp. °C	k	Temp. coeff.	Energy of activation.
15	0·004635		
		2·227	21960 cals
25	0·010526		
		2·044	13040 „
35	0·021516		
		1·85	11260 „
45	0·03976		
		1·772	10470 „
55	0·07050		

with increase of temperature the energy of activation decreases as required.

Induction Factor

When manganese sulphate is added to a reaction mixture containing sec-Butyl alcohol and chromic acid in presence of $HClO_4$ the velocity of the reaction decreases and as the reaction proceeds a brown precipitate of MnO_2 appears. Chromic acid in presence of acid does not oxidise manganese sulphate to manganese dioxide; here the sec-Butyl alcohol induces the oxidation of mangansee

sulphate to manganese dioxide. Several other examples of such induced oxidations have been studied by other workers. Some detailed studies have been made by Schonbein,[15] Manchot,[16] De Lury,[17] Luther and Rutter,[18] and Watanabe and Westheimer.[19]

According to the accepted terminology chromic acid is the actor, sec-Butyl alcohol the inductor, and manganese sulphate the acceptor; induction factor is defined as the ratio of the no. of equivalents of the acceptor oxidised to the no. of equivalents of the inductor oxidised. During the reaction a substance or ion which is a more powerful oxidiser than the actor is probably formed which then oxidises the acceptor. A study of the induced reaction and determination of the induction factor very often leads to the identification of this intermediate substance formed.

In all the induced reactions involving chromium so far studied the induction factor has been found to be either 0·5 or 2·0. This means that of the three equivalents of chromic acid present, either one or two are utilised by the acceptor while the remaining two or one are utilised by the inductor; thus in an induced reaction involving chromic acid as the actor, the only two possible values for the induction factor are 0·5 and 2·0. But these two values, it has been found are obtained only as a limit, usually values smaller than these are obtained.

EXPERIMENTAL PROCEDURE

Definite amounts of alcohol, acid, perchloric acid and manganese sulphate were pipetted out into Erlenmeyer flasks in the required concentrations and the reaction allowed to proceed to completion. The manganese dioxide is then filtered off through a gooch crucible and analysed by digesting with known amount of sodium oxalate solution and titrating the excess oxalate against standard permanganate solution. The chromic acid content of the filtrate is estimated iodometrically. From the manganese dioxide the amount of manganese sulphate oxidised is obtained and alcohol oxidised is known from the amount added, from these the induction factor is calculated. Results are given below:

Table VI. Induction factor

A. HClO$_4$ 0·2 M ; M$_n$SO$_4$ 0·4 M ; Temp. 30°C   Time 30 hrs.

No.	No. of eqts. of alcohol oxidised	No. of eqts. of MnSO$_4$ oxidised	Induction factor.
1.	0·00367	0·00124	0·35
2.	0·00897	0·00270	0·30
3.	0·01075	0·00454	0·42
4.	0·01424	0·00625	0·44
5.	0·01807	0·00639	0·35
6.	0·01900	0·00720	0·41
7.	0·0226	0·00639	0·33
8.	0·03107	0·00777	0·25
9.	0·03400	0·00799	0·23
10.	0·04090	0·00988	0·24

B. HClO$_4$ 0·2 M ; MnSO$_4$ 0·2 M.   Temp. 30°C.   Time 40 hrs.

No.	No. of eqts. of alcohol oxidised	No. of eqts. of MnSO$_4$ oxidised	Induction factor.
1.	0·0063	0·00105	0·16
2.	0·01124	0·00234	0·21
3.	0·0155	0·00355	0·23
4.	0·01867	0·00613	0·00
5.	0·02664	0·00613	0·23
6.	0·0335	0·00712	0·21

C. HClO$_4$ 0·2 M ; MnSO$_4$ 0·4 M ; Temp. 20°C ; Time 75 hrs.

No.	No. of eqts. of alcohol oxidised	No. of eqts. of MnSO$_4$ oxidised	Induction factor.
1.	0·001076	0·00029	0·27
2.	0·002152	0·00053	0·25
3.	0·003228	0·00067	0·21
4.	0·004304	0·00082	0·19
5.	0·005380	0·00091	0·17
6.	0·006456	0·0010	0·16

D. HClO$_4$ 0·2 M ; MnSO$_4$ 0·4 M ; Temp. 20°C ; Time 60 hrs.

No.	No. of eqts. of alcohol oxidised	No. of eqts. of MnSO$_4$ oxidised	Induction factor.
1.	0·001076	0·00031	0·32
2.	0·002152	0·00048	0·23
3.	0·003228	0·000595	0·20

E. $HClO_4$ 0.2 M ; $MnSO_4$ 0.4 M ; Temp. 20º C ; Time 65 hrs.

No.	No. of eqts. of alcohol oxidised	No. of eqts. of $MnSO_4$ oxidised (from M_nO_2)	Induction factor I.	Induction factor II.
1.	0.001614	0.00048	0.31	0.44
2.	0.002152	0.000545	0.26	0.31
3.	0.00269	0.00058	0.22	0.29
4.	0.003228	0.00069	0.21	0.28

In series A and B, the alcohol oxidised has been calculated from the amount of chromic acid reduced ; in C, D and E the alcohol added is taken to be completely oxidised. In series E the dissolved manganese dioxide was also taken into account in calculating the total amount of manganese dioxide formed. The method of Lang and Zwerina[20] was followed with slight modification. Here the chromic acid content of the filtrate was determined by iodometric titration. Then the chromic acid content of another portion, after reducing the manganic salt to the manganous state was determined again by iodometric titration. The difference gives the amount of MnO_2 dissolved. This was added to the amount of MnO_2 determined from the filter residue. Induction factor I has been calculated from the MnO_2 obtained in the filter residue only ; In the calculation of induction factor II, the total MnO_2 formed, dissolved as well as that obtained from the filter residue has been taken into account.

The maximum value for the induction factor in the above series is 0.44. Though this is slightly less than the limiting value 0.5, since the only possible values are 0.5 and 2.0 it is beyond doubt that the limiting value in this case is 0.5. This means that the intermediate ion of chromium formed in this reaction is Cr.^{IV}.

Taking into account this conclusion the following mechanism for the oxidation of sec-Butyl alcohol in presence of manganese sulphate may be proposed.

$$HCrO_4 + CH_3-CH_2-CHOH-CH_3 \rightarrow Cr^{IV} + CH_3-CH_2-CO-CH_3$$
$$2Cr^{IV} + Mn^{II} \rightarrow 2Cr^{III} + Mn^{IV}.$$
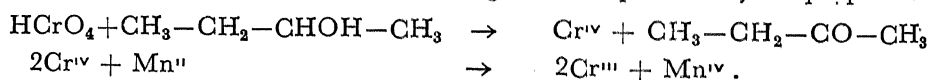
For the oxidation of sec-Butyl alcohol in the absence of manganese sulphate the following mechanism can be proposed :

$$HCrO_4^- + CH_3-CH_2-CHOH-CH_3 \rightarrow Cr^{IV} + CH_3-CH_2-CO-CH_3. \quad (a)$$

and $2Cr^{IV} + CH_3-CH_2-CHOH-CH_3 \rightarrow 2Cr^{III} + CH_3-CH_2-CO-CH_3.$ (b)

or, $Cr^{IV} + CH_3-CH_2-CHOH-CH_3 \rightarrow Cr^{II} + CH_3-CH_2-CO-CH_3.$ (c)

and $Cr^{II} + Cr^{VI} \rightarrow Cr^{III} + Cr^{V}.$ (d)

and $Cr^{V} + CH_3-CH_2-CHOH-CH_3 \rightarrow Cr^{III} + CH_3-CH_2-CO-CH_3.$ (e)
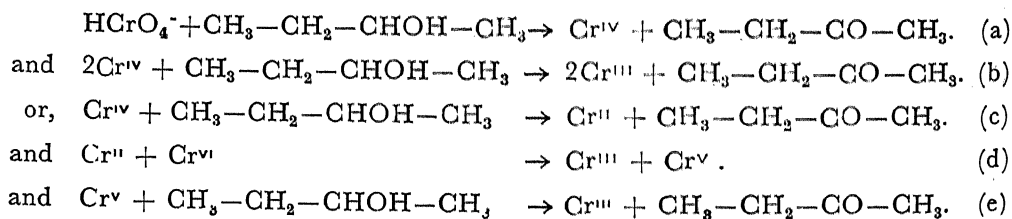
The second formulation (a, c, d and e) is similar to the one proposed by Westheimer for iso-Propyl alcohol, but this necessitates the assumption that Cr^v is also formed during the reaction whereas the first one, (a and b) does not require such an assumption.

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KINETICS OF THE OXIDATION OF AMINE BY HYDROGEN PEROXIDE

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INTRODUCTION

The problem of amine oxidation is similar to that of the formation of sulphoxides[1] or sulphones and while a large volume of literature exists on the subject little of it clarifies the kinetic mechanism of the reaction. Thus it is well-known that hydrogen peroxide cleanly oxidises tertiary amines to form amine oxide[2] and in case of secondary or primary amine groups the end product is hydroxylamine.[3] Early researches were confined to the isolation of the reaction products. As a general case for the oxidation of amines, an electron-transfer mechanism has been postulated by Horner[4] which leads to free radicals arising from both amine and peroxide. A study of the reaction between amine and benzoyl peroxide by Nozaki and Bartlett[5] indicated the formation of free radicals who found that the decomposition of benzoyl peroxide in presence of the amine shows a slight inhibiting tendency of oxygen.

It was Ross,[6] who first tried to determine the rate constants for the oxidation of tertiary amine with hydrogen peroxide in aqueous solution but in non-aqueous media this has hardly been carried out so far. This is probably due to the difficulty of having the peroxide in non-aqueous solvents. Moreover Ross[6] determined the rate of the disappearance of the peroxide and therefrom calculated the rate constant for amine oxidation which leads one to the conclusion that all the peroxide decomposed is stoicheiometrically consumed in the process of oxidation. That this is not so is found by actually estimating both the amine and the peroxide at a particular time in a run. Hence the determination of the kinetic constants for the oxidation of tertiary amine is of sufficient interest which led us to undertake this systematic study of the reaction and this communication reports our results.

EXPERIMENTAL

Triethylamine and Solvents.—Triethylamine was purified by the usual method, distilled twice in all glass set collecting the fraction having a boiling range of 89·5—90°C.

Solvents of A. R. quality were purified and dried by the usual method and finally distilled twice in all-glass set.

Preparation of the Peroxide Solution.—Strong aqueous hydrogen peroxide (E. Merck 30 %) was mixed with distilled pure solvent and shaken vigorously. The aqueous layer was then separated and the peroxide solution in the solvent was dried repeatedly with pure anhydrous sodium sulphate keeping the whole content *in*

a refrigerator. The solution was then titrated iodometrically and the hydrogen peroxide content was determined therefrom. This stock solution was then diluted to any desired concentration and used in the reaction.

Estimation of the Amine.—Amine was estimated by non-aqueous titration in glycol-isopropanol mixture as recommended by Palit[7] against standard perchloric acid in the same medium, with bromophenol blue as indicator.

Technique.—Experiments were carried out at temperatures of 50° and 60°C.±0·1°C.

Stoppered flasks were used for the reaction. Required amounts of the amine and the peroxide solution were added, mixed and kept at the required temperature 6 c.c. of the reaction mixture was pipetted out, at the required interval, of which 1 c.c. was added to 10 c.c. of 2N sulphuric acid in which potassium iodide has been dissolved and the corresponding amount of the peroxide was determined by the usual iodometric titration. The other 5 c.c. of the reaction mixture was added to 5 c.c. of glycol-isopropanol mixture and the corresponding amount of amine was estimated by titration against standard perchloric acid.

Mechanism of the reaction.—Evidence existed that the decomposition of peroxides are greatly accelerated by the presence of amine. That a solution of benzoyl peroxide in amine decomposes almost explosively was noticed by Nozaki and Bartlett.[8] But it was not certain whether an equivalent amount of the amine is oxidized by every molecule of the peroxide undergoing decomposition. Experimental determination of the reaction already evidenced that for a certain period of time, the amount of peroxide undergoing decomposition is much faster than that of the amine itself. Table I verifies one such determination.

Table I

Rates of Decomposition and Oxidation Reaction in the Triethyl Amine—Hydrogen Peroxide system in Propyl Acetate at 50° and 60°C.

Temperature °C.	Time in hrs.	% H₂O₂ Decomposition.	% Amine Reacted.
50·0	0·5	3·33	0·90
	1·5	15·00	1·75
	4·0	35·00	3·15
	8·0	60·00	5·29
	27·0	95·00	8·11
60·0	0·5	11·11	2·06
	1·0	20·64	3·53
	2·0	36·51	5·00
	4·0	58·73	6·59
	6·0	74·61	8·00
	8·0	82·54	9·12

Hence it is quite clear that no single reaction is predominant but the whole scheme is composed of a number of reactions. From our results to be reported the reaction appears to take the course.
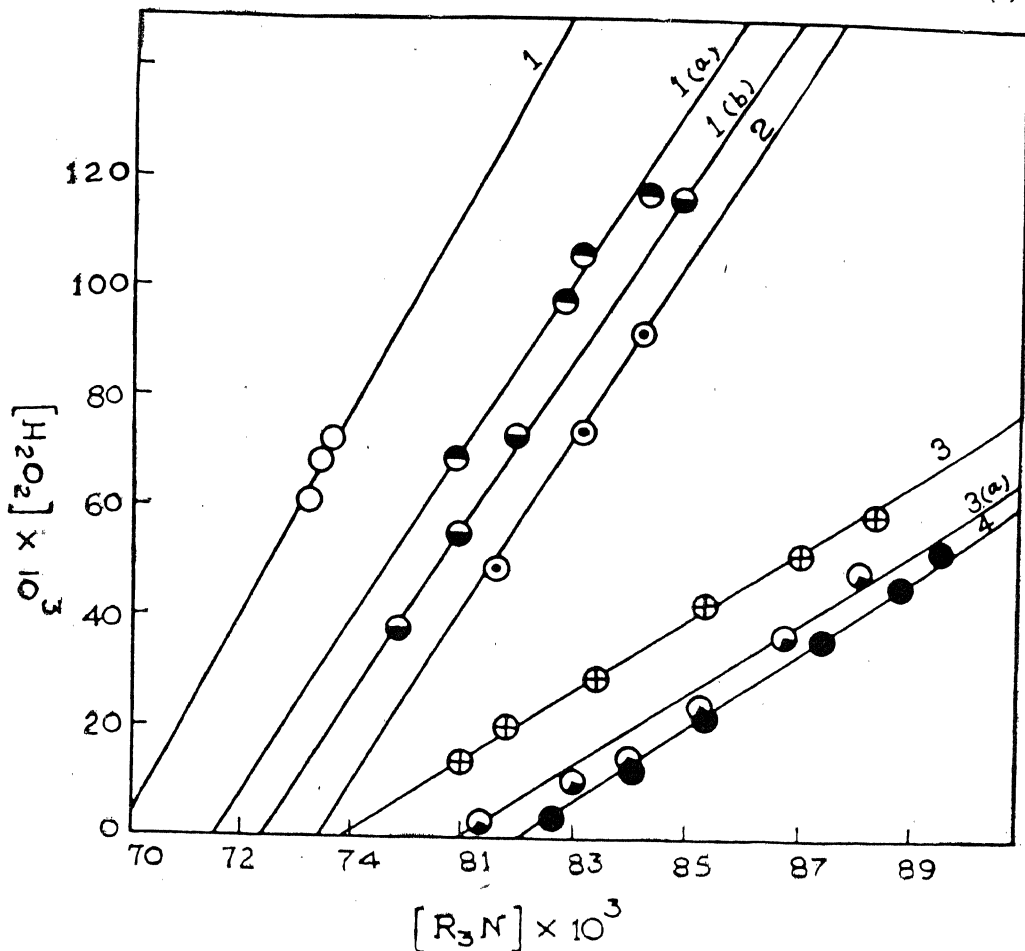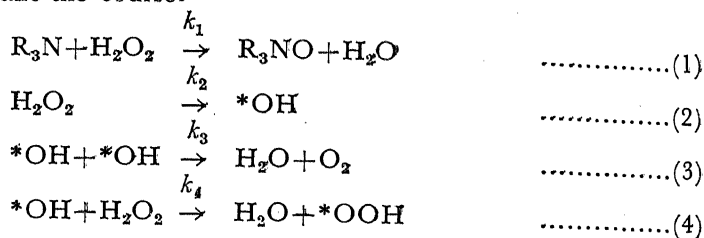
$$R_3N+H_2O_2 \xrightarrow{k_1} R_3NO+H_2O \qquad \dots\dots\dots(1)$$

$$H_2O_2 \xrightarrow{k_2} *OH \qquad \dots\dots\dots(2)$$

$$*OH+*OH \xrightarrow{k_3} H_2O+O_2 \qquad \dots\dots\dots(3)$$

$$*OH+H_2O_2 \xrightarrow{k_4} H_2O+*OOH \qquad \dots\dots\dots(4)$$

Fig. 1.—Determination of the value of 'n'.
1. 1 (a), 1 (b)—Ethyl Acetate — 60°C.
2.   —Ethyl Acetate — 50°C.
3.   (a)   —Propyl Acetate— 60°C.
4.   —Propyl Acetate— 50°C.

In the first step the oxidation of the R_3N is a direct product of the type $R_3N(OH^+)(OH^-)$ from which an amine oxide is produced by dehydration.[9] The hydrogen peroxide at the same time undergoes a free radical type of decomposition and in actual practice the velocity of the first reaction is much slower than the induced decomposition of H_2O_2 (sum total of reactions (2), (3) and (4)).

Let n molecules of hydrogen peroxide decompose within a period when one molecule of the hydrogen peroxide carries on the oxidation reaction. Hence the velocity of reaction No. 1 is $1/n$ times of that of the total decomposition of the peroxide. Hence the plot of the concentration of the hydrogen peroxide against that of the amine at a time t will give the value of n from the slope. Fig. 1 shows the result of such determination.

The rate for the oxidation can now be represented by

$$-\frac{dx}{dt} = [k_1[R_3N][H_2O_2] \qquad \dots\dots\dots\dots(5)$$

where 'x' denotes the amount of R_3N consumed. Let 'a' and 'b' denote the initial concentration of the amine and hydrogen peroxide respectively. Then the rate can be written as

$$-\frac{dx}{dt} = k_1(a-x)(b-nx) \qquad \dots\dots\dots\dots(6)$$

which on integration takes the form

$$k_1 t = \frac{1}{n\left(a - \frac{b}{n}\right)} \log_e \frac{b(a-x)}{a(b-nx)} \qquad \dots\dots\dots\dots(7)$$

$$\text{or} \quad \log \frac{(a-x)}{(b-nx)} = \frac{(na-b)}{2\cdot303} k_1 t - \log \frac{b}{a} \qquad \dots\dots\dots\dots(8)$$

Hence the plot of $\log\{(a-x)/(b-nx)\}$ against 't' will be straight line from the slope of which k_1 can easily be calculated.

Coming to the decomposition of the hydrogen peroxide we can write,

$$-\frac{d[H_2O_2]}{dt} = k_1[R_3N][H_2O_2] + k_2[H_2O_2] + k_4[OH][H_2O_2] \dots\dots\dots\dots(9)$$

for the rate of disappearance of the peroxide. The concentration of the free radicals $*OH$ can be written as

$$[*OH] = \sqrt{\frac{k_2 H}{k_3}} \qquad \dots\dots\dots\dots(10)$$

where H denotes the concentration of the hydrogen peroxide. Equation (9) then reduces to the form

$$-\frac{dH}{dt} = k_2[H] + k_4 \sqrt{\frac{k_2}{k_3}} [H]^{3/2} + k_1[R_3N][H] \qquad \dots\dots\dots\dots(11)$$

The last term in equation (11) i.e., $k_1[R_3N][H]$ is the velocity of the oxidation of the amine which is $1/n$ times of that of the total peroxide decomposition. Hence we can write it in the form

$$- \frac{dH}{dt} = \left\{ \frac{n+1}{n} \right\} \left\{ k_2[H]^{\frac{1}{2}} + k_i[H]^{3/2} \right\} \quad \dotfill (12)$$

where k_i stands for $k_4 \sqrt{\frac{k_2}{k_3}}$.

Integrating equation No. (12) we get.

$$\ln \frac{k_2 + k_i\sqrt{H}}{k_i\sqrt{H}} - \ln \frac{k_2 + k_i\sqrt{H_o}}{k_i\sqrt{H_o}} = \frac{k_2 \cdot t(n+1)}{2n} \quad \dotfill (13)$$

or

$$\ln \frac{c + \sqrt{H}}{\sqrt{H}} - \ln \frac{c + \sqrt{H_o}}{\sqrt{H_o}} = \frac{k_2 \cdot t(n+1)}{2n} \quad \dotfill (14)$$

where $c = \frac{k_2}{k_1}$.

This is the same form as that of Nozaki and Bartlett[8] used in determining the rate constants for the decomposition of benzoyl peroxide. If H_1 and H are the peroxide concentrations at equal times in the two runs, one obtains

$$\ln \frac{c + \sqrt{H_1}}{\sqrt{H_1}} - \ln \frac{c + \sqrt{H_2}}{\sqrt{H_2}} = \ln D \quad \dotfill (15)$$

which may be converted to the form

$$\frac{1}{\sqrt{H_1}} = \frac{D}{\sqrt{H_2}} + \frac{D-1}{c} \quad \dotfill (16)$$

From a plot of $\frac{1}{\sqrt{H_1}}$ against $\frac{1}{\sqrt{H_2}}$ a straight line should be obtained from whose slope and y intercept c can be calculated. Once c being evaluated equation (14) can be utilised for the determination of k_2. The plot of $\ln \frac{c + \sqrt{H}}{\sqrt{H}}$ against 't' will give a straight line from whose slope k_2 can be evaluated which in turn yield the value of k_1 from the value of c.

Rate Constants for the amine Oxidation.—Reaction was carried out in ethylacetate and propylacetate as solvent at temperatures of 50° and 60°C. Experimental results were found to be in excellent agreement with the mechanism just suggested. Some of the typical results are represented in Fig. 2 and Tables II and III. The value of n was determined from the plot of the concentration of the peroxide

against that for the amine at a time 't' and they have already been represented in Fig. I. It is found that the value n is near about constant for a certain solvent and is not much affected by a change of temperature also. Thus with different runs having a different concentration of the components, the value of k_1 is found to be sensibly constant. The value of the rate constant in case of propyl acetate is about ten times than that in case of ethyl acetate at both the temperatures. The temperature variation of k_1 and the corresponding energy of activation has also been calculated and they are found to be very little different in the two solvents studied.

Table II

Determination of the Rate Constant for the Oxidation of the Amine by Hydrogen Peroxide in Propyl Acetate at temperatures of 50° and 60°C.

Temperature °C.	Time in hrs.	(Conc. of $H_2O_2) \times 10^2$ mols.	(Conc. of Amine) $\times 10^2$ inn mols.	n	Rate Const. k_1^* in m/l/sec.	Energy of Activation E_{k_1} in kcals.
50·0	0·0	5·48	9·56			
	0·5	5·29	9·45			
	1·5	4·65	9·37	7·0	$4·92 \times 10^{-5}$	
	4·0	3·56	9·23			
	8·0	2·19	9·03			
	27·0	0·33	8·76			
60·0	0·0	5·75	9·13			
	0·5	5·11	8·94			
	1·0	4·93	8·80			
	2·0	3·65	8·67			
	4·0	2·37	8·52	7·1	$9·72 \times 10^{-5}$	13·82
	6·0	1·46	8·40			
	8·0	1·00	8·29			
	30·0	0·27	8·13			
60·0	0·0	5·89	8·32			
	0·5	5·20	8·19			
	1·5	4·29	8·02			
	3·5	2·92	7·83	6·7	$9·08 \times 10^{-5}$	
	5·5	2·00	7·68			
	7·5	1·37	7.59			
	30·5	0·23	7·35			

*Calculated from the slope of the plot of $log\ (a-x)/(b-nx)$ against t and from the relation $k_1 = slope \times 2.303/(na-b)$.

Table III
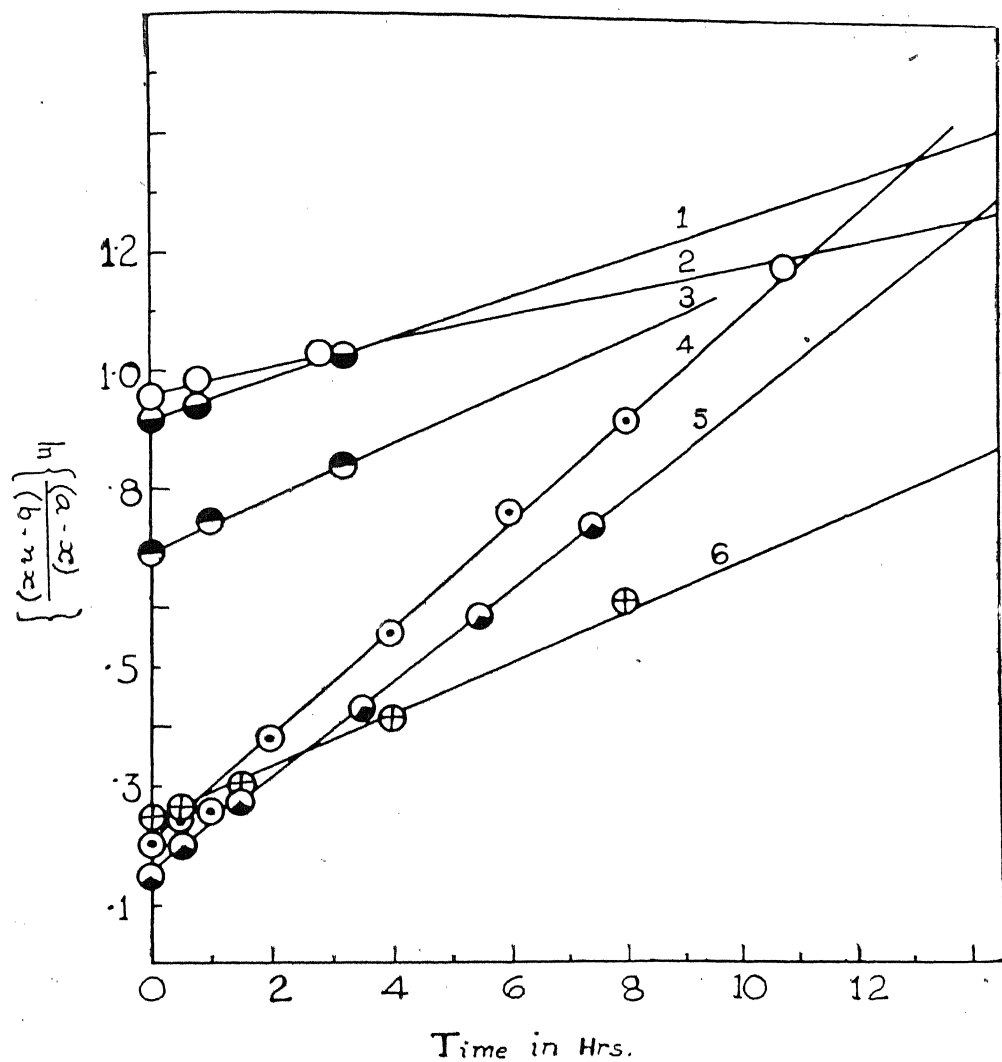
Determination of the Rate Constant for the Oxidation of the Amine by Hydrogen Peroxide in Ethyl Acetate at 50° and 60°C.

Temperature °C.	Time in hrs.	(Conc. of $H_2O_2) \times 10^2$ mols.	(Conc. of Amine) $\times 10^2$ in mols.	n	Rate Const. k_1* m/l/sec.	Energy of Activation E_{k_1} in kcals.
50·0	0·0	11·64	10·42			
	2·0	10·67	10·30			
	7·0	9·70	10·27	16·2	$4·749 \times 10^{-6}$	
	28·0	6·79	10·08			
	52·0	3·39	9·77			
60·0	0.0	9·80	8·07			
	2·0	9·19	7·92			
	8·0	7·35	7·82	16·6	$9·54 \times 10^{-6}$	14·81
	28·0	4·90	7·66			
	52·0	1·99	7·57			
60·0	0·0	17·16	8·48			
	2·5	14·7o	8·23			
	8·0	11·64	7·98	15·7	$9·45 \times 10^{-6}$	
	27·5	7·35	7·68			
	51·5	5·51	7·58			

*Calculated from the slope of the plot of *log* $(a-x)/(b-nx)$ against t and from the relation $k_1 = (\text{slope} \times 2·303)/(na-b)$.

Fig. 2.—Determination of the rate constant (k_1) for the oxidation of the Amine.

1, 3.—Ethyl Acetate — 60°C.
2.—Ethyl Acetate — 50°C.
4, 5.—Propyl Acetate — 60°C.
6.—Propyl Acetate — 50°C.

Rate Constants for Hydrogen Peroxide Decomposition.—The rate constants k_2 and k_1 for hydrogen peroxide in the solvents studied was determined by the procedure described previously. The value of c was determined from the plot of $\dfrac{1}{\sqrt{H_1}}$ against

$\dfrac{1}{\sqrt{H_2}}$ and they are represented in Fig. 3. Evaluation of c was utilised in the deter-
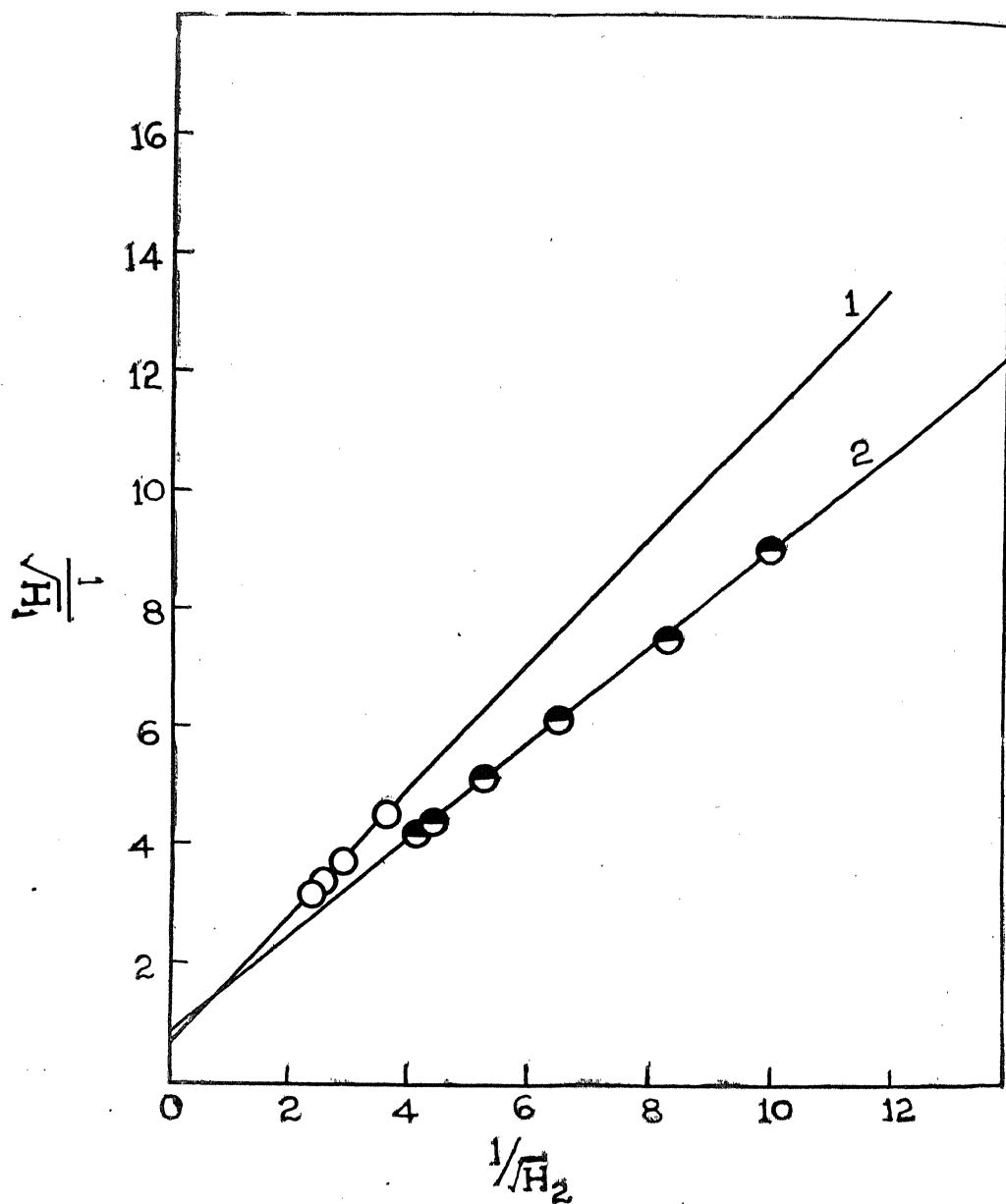
Fig. 3.—Determination of the value of 'C'.

1.—Ethyl Acetate.

2.—Propyl Acetate.

mination of k_2 by plotting $\ln \dfrac{c+\sqrt{H}}{\sqrt{H}}$ against t and k_2 was determined from the slope of the straight line obtained. Fig. 4 and Table IV represents the results. In case of propyl acetate the value of the rate constants k_2 and k_1 are both higher than that in ethyl acetate. The same trend is also noticed in the case of the value of the rate constant for the oxidation reaction.
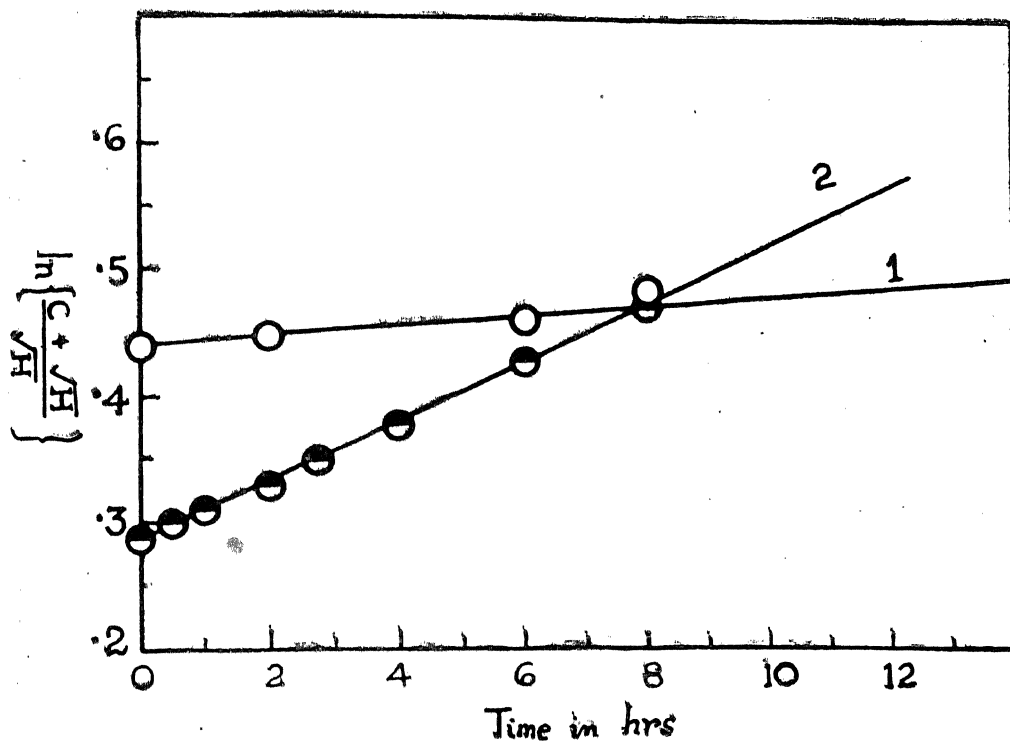
Fig. 4.—Determination of the rate constant (k_2) for the decomposition of Hydrogen Peroxide.

1.—Ethyl Acetate.

2.—Propyl Acetate.

Table IV

Determination of the Rate Constants in the Decomposition of Hydrogen Peroxide in Ethyl and Propyl Acetate at 60°C.

Solvent.	Temperature °C.	n	c $(=k_2/k_1)$	k_1^* $m/1/hr.$	k_1^{**} $(m/1)^{\frac{1}{2}}$ hrs.$^{-1}$
Ethyl Acetate	60·0	16·0	0·167	0·0075	0·0432
Propyl Acetate	60·0	7·0	0.227	0·a410	0·1840

*Calculated from the slope of the plot of *loy* $(c+H)/H$ against t.
**Calculated from the relation $c = k_2/k_1$.

DISCUSSION

It is apparent from the preceding results that the reaction between tertiary amine and hydrogen peroxide is not a simple reaction of the ordinary type but is composed of a number of reactions undergoing simultaneously. The mechanism suggested previously is supported by the experimental results. Apart from the first reaction of the formation of amine oxide which is well-known and has been widely studied the reaction scheme is composed of the free radical type of decomposition of the peroxide. This is supported by the fact that the decomposition of the peroxide in the presence of amine, also, is inhibited by the presence of oxygen. Moreover at a constant concentration of the amine the percent decomposition of the peroxide at different concentrations varies, which shows that the decomposition is not a unimolecular reaction. This clearly evidences that the decomposition involves a reaction of the free radical type.

In case of tertiary amine, to react with hydrogen peroxide, the lone pair of the nitrogen enters the oxygen sextet and this link between the nitrogen and oxygen in the resulting amine oxide is quite strong and stable. The formation of this oxide is probably a case of the type

$$\text{dehydration}$$

$$R_3N + H_2O_2 \quad \rightarrow \quad R_3N(OH^+)(OH^-) \quad \rightarrow \quad R_3NO + H_2O$$
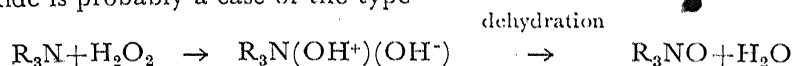
as suggested by Meisenheimer.[9] Ross[6] also supports this view on the oxidation of triethylamine with hydrogen peroxide in aqueous solution. In his case he obtained a value of $2 \cdot 0 \times 10^{-2}$ m/t/min for the rate constant of the formation of amine oxide, quite a high value in comparison to that obtained by us in case of ethyl acetate or propyl acetate. This high value in his case is probably due to the assumption that the decomposition of the peroxide is the same reaction of the formation of amine oxide which is found not to occur. Moreover in case of aqueous system it is well known that water itself acts as a catalyst in the spontaneous decomposition of the hydrogen peroxide. Table V shows the relation between the decomposition of the peroxide and the formation of amine oxide in aqueous system.

Table V

Relation between the Rates of the Oxidation Reaction and Decomposition in the Triethyl Amine—Hydrogen Peroxide system in Aqueous Solution at 50°C.

Time in hrs.	% Amine reacted.	% H_2O_2 Decomposition.
1·0	2·62	33·10
2·0	2·90	36·00
4·0	3·70	43·50
7·0	4·35	52·00

Solvent, also, undoubtedly plays an important part in the oxidation of the amine. That, in case propyl acetate the rate of the oxidation as well as the decomposition of the peroxide is much higher than that in case of ethyl acetate though the energy of activation for the first reaction is not much different in the two solvents. In this connection it is most interesting to note that the increase in the velocity of the reaction of the oxidation of the amine, is accompanied by a decrease in the value of n. So it may not be improper to assume that the lower the value of n the higher will be the velocity of the reaction leading to the formation of the amine oxide. Hence the velocity, as well as the quantitative transformation of the amine to its oxide will be maximum in a solvent where the value of n will be near about unity. A choice of such a suitable solvent will go a long way towards the problem of the quantitative preparation of amine oxide.

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STUDIES IN THE KINETICS OF THE REACTION BETWEEN HYDRO-GEN PEROXIDE AND POTASSIUM PERSULPHATE-PART II

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In part I of this paper[1] we have shown that the reaction between hydrogen peroxide and potassium persulphate in the absence of a catalyst is very slow even at 40°C but becomes of a measurable speed at 25°C and above in the presence of Ag^{+} ion as catalyst. The reaction was found to be unimolecular with respect to persulphate ion and independent of the concentration of hydrogen peroxide. It was found to be dependent on the concentration of Ag^{+} ion. The addition of H_2SO_4 was found to retard the reaction. In that paper the temperature coefficient was also determined, the value of which for 10° difference in temperature was found to be 1·69.

In the persent paper we have studied the effect of variation of H_2O_2 concentration and of $K_2S_2O_8$ concentration in greater detail to confirm our previous conclusions. The catalytic effect of copper sulphate has also been studied. The salt effect has been investigated in the presence of following electrolytes *e. g.* potassium sulphate, ammonium sulphate, sodium sulphate, sulphuric acid, magnesium sulphate and manganous sulphate. The effect of the non-electrolyte urea has also been studied. Incidentally it may be mentioned that some observations on the kinetics of the uncatalysed reaction between H_2O_2 and $K_2S_2O_8$ have been previously made by Friend.[2]

The object of the present study has been to find out if there is any similarity in behaviour of this reaction with other reactions involving persulphate ion and to elucidate a general mechanism for all reactions in which persulphate ion is the oxidising agent. In this connection we have previously studied the oxidation of oxalic acid by persulphate ion[3] and the oxidation of formate ion by persulphate ion.[4] A critical study of these reactions and other reactions of persulphate ion leads us to conclude that all such reactions follow a general mechanism put forward by us.

EXPERIMENTAL

The experimental technique and details are the same as followed in part I of this paper. All the salts used for the study of salt effect were of A.R. B.D.H. quality and as before the solutions were always prepared in redistilled water from a quartz distilling flask.

RESULTS OF THE MEASUREMENTS

Effect of hydrogen peroxide concentration.—The reaction was performed with different initial concentrations of H_2O_2, keeping the concentration of $K_2S_2O_8$ and $AgNO_3$ constant.

Table. 1

$K_2S_2O_8 = 0.01$ M ; $AgNO_3 = 0.0002$ M ;   Temperature $= 30°C$

Concentration of H_2O_2	Time for the decomposition of 3 c. c. of N/50 H_2O_2	K Unimolecular (mean value)
0·01M	49 min.	0·019405
0·04M	48·5 min.	0·01933
0·06M	48·0 min.	0·02048
0·10M	45·0 min.	0·02055

From the above table it is clear that there is no effect of H_2O_2 concentration on the velocity of this silver-catalysed reaction because even an increase of ten times in the concentration of H_2O_2 does not result in any appreciable change in the time required for the decomposition of a certain amount of H_2O_2.

Effect of $K_2S_2O_8$ Concentration.—The concentration of $K_2S_2O_8$ was increased 2½ times that of H_2O_2 , in order to study the effect of $K_2S_2O_8$ concentration on this reaction.

Table 2

$K_2S_2O_8$ = 0·025M

H_2O_2 = 0· 01M

$AgNO_3$ = 0·00015M   Temperature $= 30°C$

Time in minutes	Volume of N/50 $KMnO_4$ in c. c.	Volume of N/50 $KMnO_4$ corresponding to $K_2S_2O_8$ Concen.	K Unimolecular
1	4·87	12·37	
5	4·18	11·68	0·01428
10	3·42	10·92	0·01384
15	2·55	10·05	0·01484
20	1·84	9·34	0·01479
25·5	1·22	8·72	0·01427
32·0	0·47	7·97	0·01418
		mean	0·01433

A comparison of the above table with table 2 of Part I of this paper shows that the velocity constant has only slightly increased by increasing the concentration of potassium persulphate by 2½ times. (mean Values being 0·013398 and 0·01433 respectively). This slight increase may be attributed to any trace of impurity or to a very slight increase in the concentration of the catalyst silver nitrate. While we observe that the rate of decomposition has increased greatly, the time for the decomposition of potassium persulphate corresponding to 3 c. c. of N/150 $KMnO_4$ being about 18 minutes only instead of about 50 minutes with 0·01M $K_2S_2O_8$ concentration.

Catalytic Effect of Copper Sulphate.—Copper sulphate has been found to be a powerful catalyst in most of the reactions of persulphate ion [4],[5]. Its catalytic effect on this reaction has also been studied.

Table 3

$K_2S_2O_8$=0·01 M ;	H_2O_2=0·01M ;	Temperature=30°C $CuSO_4$=0·002 M.
Time in minutes	Volume of N/50 $KMnO_4$ in c.c.	K Unimolecular
1	4·82	
5	4·53	0·01549
10	4·28	0·01320
15	4·18	0·01280
25	4·09	0·006839
40	3·82	0·005957
61	3·64	0·004679
90	3·28	0·004324
120	3·01	0·003956
150	2·77	0·003718
180	2·60	0·003447
210	2·56	0·003029

We have seen previously (in Part I of this paper) that in the absence of any catalyst the reaction even at 40°C. is very slow, the velocity constant with 0·025 M $K_2S_2O_8$ being only 0·0003245. Thus it is clear from the above table that $CuSO_4$ catalyses this reaction also. We, however, note that:—

(1) The catalytic activity of copper sulphate in this reaction is much less than that of silver nitrate.

(2) The unimolecular constant decreases with time continuously. This suggests that either the concentration of $CuSO_4$ goes down with time due to some secondary reactions which results in a decrease of the reaction rate with

time, or the catalytic activity of copper sulphate is due to chain reaction and the decrease in reaction rate with time is due to the breaking up of chains as the reaction proceeds.

In this connection, we have made an interesing observation that if KCl is added in the presence of $CuSO_4$ to the reaction mixture in order to see the effect of halide ions, it is found that a mixture of KCl and $CuSO_4$ decomposes H_2O while neither $CuSO_4$ nor KCl alone decomposes H_2O_2.

Salt Effect.—The salt effect was studied with the following electrolytes *viz*, K_2SO_4, H_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, and $MnSO_4$, the results of which are summarized in the following table.

Table 4

$K_2S_2O_8 = 0.01M$;	$H_2O_2 = 0.01M$;
$AgNO_3 = 0.0002M.$	Temperature $= 30°C$

Ionic Strength μ	Electrolyte added	K Unimolecular (Average value)
0.0302	—	0.019405
0.3302	K_2SO_4	0.01088
0.3302	Na_2SO_4	0.01267
0.3302	$(NH_4)_2SO_4$	0.01666
0.2802	$MgSO_4$	0.01299
0.2802	$MnSO_4$	0.01028
0.3302	H_2SO_4	0.01130

We find that the reaction rate is decreased with increase in ionic strength due to the addition of different electrolytes and this decrease in reaction rate by different electrolytes at the same ionic strength is of the same order except in the case of ammonium sulphate. This may be due to the catalytic effect of ammonium ion as it is known to catalyses other reactions involving persulphate ion.

A decrease in the reaction rate in the presence of different electrolytes investigated by us leaves no doubt that the electrolytes have a negative salt effect on this reaction. Now the question is whether this negative salt effect is due to the rate determining reaction between two oppositely charged ions or between a charged ion and a neutral molecule. In the former case the logarithm of the specific reaction constant should be directly proportional to the square root of ionic strength *i.e.*, *log* $K \propto \sqrt{\mu}$ where K is the specific reaction constant at an ionic strength of μ, while in the latter case the reaction constant should have a linear relationship with the ionic strength.

To decide the nature of the negative salt effect the reaction was studied at different ionic strength with potassium sulphate as the added electrolyte. The experimental results with different concentrations of potassium sulphate are summarised in the following table :—

Table 5

$K_2S_2O_8 = \cdot 01M$; $H_2O_2 = \cdot 01M$,   Temp. $= 30°C$
$AgNO_3 = 0 \cdot 0002M$

Conc. of K_2SO_4	Ionic strength μ	$\sqrt{\mu}$	K Unimolecular (average)	Log K
0·1M	·3302	·5746	·01088	−1·9633
0·05M	·1802	·4254	·012421	−1·9059
0·15M	·4802	·6930	·0095052	−2·0218
0·20M	·6302	·7939	·008313	−2·0802

On plotting $\sqrt{\mu}$ against Log K from the above table it is found that a straight line with a negative slope is obtained which indicates a linear relationship between log K and $\sqrt{\mu}$ and leads in to believe that the rate determining reaction is between two oppositely charged ions.

Effect of Non-electrolyte—Urea.—In other reactions of persulphate ion studied by us (*loc. cit*) we have seen that urea inhibits the reactions in question. We have found that this reaction is also inhibited by urea, a fact which strengthens our belief that generally all reactions involving persulphate ion follow a similar mechanism. The results showing the inhibitory effect of urea on this reaction are recorded in the following table.

Table 6

$K_2S_2O_8 = 0 \cdot 01M$; $H_2O_2 = 0 \cdot 01M$ Temp. $= 30°C$
$AgNO_3 = 0 \cdot 0002M$; Urea $= 0 \cdot 1M$

Time in minutes	Volume of N/50 $KMnO_4$ in c.c	K Unimolecular
1	5·00	
5	4·98	0·001036
10	4·95	0·001126
25	4·79	0·001794
40	4·54	0·002474
60	4·20	0·002959
80	3.80	0·003475
100	3·44	0·003779
120	3·22	0·003698
150	2·86	0·003750
200	2·40	0·003689

The unimolecular constant, however, instead of decreasing with time, as is usually the case, increases with time.

DISCUSSION

The silver-catalyzed reaction between potassium persulphate and hydrogen peroxide follows an unimolecular behaviour, being independent of the initial concentration of hydrogen peroxide and dependent upon the initial concentration of potassium persulphate and silver nitrate. There exists a linear relationship between the reaction constant and the concentration of silver nitrate. Therefore the reaction velocity is directly proportional to the first power of silver ion concentration, while, as shown before, the reaction is unimolecular with respect to persulphate ion concentration. Hence we can write

$$\frac{dx}{dt} = K \; [\, Ag^+ \,] \times [\, S_2O_8'' \,]$$

It is worthwhile to point out that this conclusion *i.e.*, the dependence of the reaction rate on the concentration of the silver ion and the persulphate ion and independence of the concentration of the reducing substance has also been reached by previous workers [6,7,8,9] in the study of other reactions of persulphate ions.
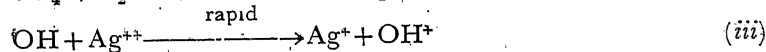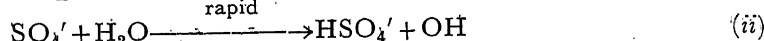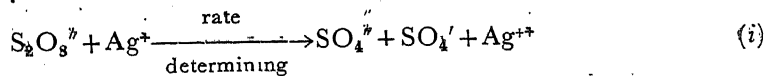
Like other reactions involving persulphate ion, this reaction is also greatly catalyzed by silver and cupric ions. Yost (*loc. cit*) has given the mechanism for reactions of persulphate ion catalyzed by silver ion wherein he has supposed the formation of trivalent silver ion according to the following equation :

$$Ag^+ + S_2O_8'' \longrightarrow 2SO_4'' + Ag^{+++}$$
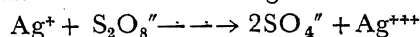
It involves a two electron-transfer in one step which does not seem to be feasible in the light of the view for ionic reactions developed by Haber and Weiss[10] and Evans[11], so that redox reactions generally involve one electron transfer in one step.

It is interesting to note from the results of other workers and also from investigations carried out be us on persulphate reactions that the general features of the silver catalyzed reactions are the same as those of the uncatalyzed reactions.

In order to explain the observed results obtained by us in the silver catalyzed reaction between potassium persulphate and hydrogen peroxide, we propose the following general mechanism for the silver-catalyzed reactions involving persulphate ion :—

$$S_2O_8'' + Ag^+ \xrightarrow[\text{determining}]{\text{rate}} SO_4'' + SO_4' + Ag^{++} \qquad (i)$$

$$SO_4' + H_2O \xrightarrow{\text{rapid}} HSO_4' + OH \qquad (ii)$$

$$OH + Ag^{++} \xrightarrow{\text{rapid}} Ag^+ + OH^+ \qquad (iii)$$

$$OH^+ + H_2O_2 \xrightarrow{\text{rapid}} O_2 + H_2O_2 + H^+ \qquad (iv)$$

Over-all reaction—$S_2O_8'' + Ag^+ + H_2O_2 \rightarrow H_2SO_4 + SO_4'' + Ag^+ + O_2$ $\qquad (v)$
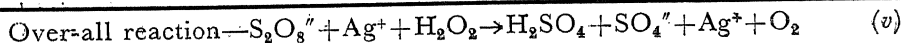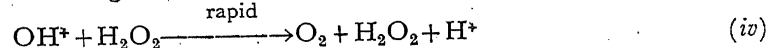
In other words, the function of silver ions is to increase the amount of active radical SO_4' which is really important in producing the radical OH^+ which is involved in the process of oxidation by persulphate ion.

This mechanism satisfactorily explains all the features of silver catalyzed reactions. Since the rate determining process is proportional to the first power of the concentration of persulphate ion, the order with respect to persulphate ion will be unity. The reaction velocity will also be proportional to the first power of the concentration of silver ion and for a given concentration of the persulphate ion the value of the constant will be directly proportional to the concentration of silver ion. The total order of the reaction will, however, still be unity which has been confirmed by us and also by other workers, i.e.,

$$-\frac{dc}{dt} = KC_{S_2O_8''} \times C_{Ag^+}$$

but since CAg^+ is constant

$$\therefore -\frac{dc}{dt} = KC_{S_2O_8''}$$

and the total order of the reaction will be unity.

We have found a negative primary exponential salt effect for this reaction, which as stated before, points out that the rate determining reaction is between two oppositely charged ions. This is confirmed by the mechanism suggested by us according to which the rate determining process is between the negatively charged persulphate ion and the positively charged silver ion.

The inhibitory effect of urea in this silver catalysed reaction is due to the removal of sulphate radical ion (SO'_4) by its interaction with urea to form some organic polymer or complex. Due to the removal of sulphate radical ion (SO_4'), OH and OH^+ are not formed so that the over-all reactions slows down. (cf. the effect of organic substrate on the reaction rate of $Fe^{++}-S_2O_8''$ reaction studied by Kolthoff and coworkers[12] and other reactions quoted by Uri[13].)

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ULTRAVIOLET ABSORPTION STUDY OF THE REACTION BETWEEN SODIUM FORMATE AND IODINE

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ABSTRACT

The course of the reaction has been followed spectrophotometrically. The increase in absorption in the ultraviolet during the initial stages prove that the loosening of the binding forces of a molecule and its light absorptive power go together.

The kinetics of the reaction between Sodium formate and Iodine in dark and light was studied by Dhar,[1] Mukherjee and Dhar,[2] Doosaj and Bhagwat,[3] Vonkiss and Urmanczy.[4] The reaction has been reported to be unimolecular with respect to both the reactants. In continuation of the study described in our earlier paper[5] this reaction was studied by us with reference to the changes in light absorption during the course of reaction. The idea is to show that during the preliminary stages of a reaction there is an increased light absorption in the ultraviolet as a result of the weakening of the bonds in the reactant molecule. This reaction is between a neutral molecule (Iodine) and an ion (formate) and the absorption changes in regions, where the formate is not having considerable absorption, are studied.

EXPERIMENTAL

The absorption spectra of $M/160$ Sodium Formate solution and $M/3520$ Iodine were separately taken by means of a Beckmann spectrophotometer. Very dilute solution of Iodine is particularly chosen because stronger solutions show complete absorption in the ultraviolet. Only aqueous solution of Iodine was taken and Potassium Iodide was avoided. Then equal volumes of $M/80$ Sod. Formate and $M/1760$ Iodine in water were mixed and immediately transferred to the absorption cell and the absorption spectra was quickly taken. Then after definite intervals of time, the absorption only at $460 m\mu$, $350 m\mu$, and $290 m\mu$, were recorded so that much time is not taken in tracing the whole curve. After a long interval of time also once more the complete spectrum is taken. The results are given in Table I.

Table I

Wavelength.	M/3520 Iodine.	M/160. Sod. Formate.	Total.	M/1760 Iodine + M/80 Sod. Formate. (Mixture in equal volumes).							
				Intervals in Minutes.							
				0	20	50	110	150	240	360	21hrs.
460 $m\mu$	50	0·5	50·5	47·5	44·5	39·0	32	27·5	21	13·0	2·5
350	30	0·1	30·1	63·0	84·0	89·0	92	9ɔ·7	86	72·5	16·0
290	44	0·1	44·1	81·5	94·5	96·5	98	97·0	95	85·0	13·0

DISCUSSION

The curve shows that the absorption spectra of Iodine alone in water has maxima at 460$m\mu$, 350$m\mu$, 290$m\mu$. Sodium formate alone shows only a continuous absorption from 230$m\mu$; its absorption in the regions 460$m\mu$, 350$m\mu$, and 290$m\mu$, being almost negligible the changes occuring at these wavelengths with time show only the fate of Iodine molecules. The absorption throughout the reaction at 460$m\mu$ is decreasing because of the reduction of Iodine concentration as the reaction proceeds. But absorption at 350$m\mu$ and 290$m\mu$ is in the initial stages more than the absorption of Iodine and Sodium formate put together.

According to our views about chemical reactivity and light absorption, whenever two substances react they must show enhanced absorption in the ultraviolet. In the earlier work by Dhar and Bhattacharya[6] the reaction was followed by a Hilger Quartz spectrograph and it could only be shown that the extreme limit of absorption was receding towards longer wavelengths in the preliminary stage. Now in this study it is found that there is no appreciable shift in the absorption maxima of Iodine in ultraviolet but only the absorption coefficient increased with time. This is not the case only for a very small amount of time immediately after mixing but persists and in fact the effect increases for a considerable length of time, after which the process becomes reversed showing less and less absorption as the products are getting accumulated. This is in keep-

ing with our idea that a primary combination between molecules predisposed to react, results in the loosening of the bond of the rectant molecules. When this loosening occurs consequent to a kind of "incipient ionisation" of the neutral molecule and the formation of a probable intermediate compound corresponding to Polanyi's "transition state,"[7] there ensues an increase of absorptive power for ultraviolet rays. Polanyi's correlation of binding strength[7] and chemical activity and Henri's observation[8] about the absorptive power of labile molecules can be put together in explaining the phenomenon that when there is increased activity there is increased light absorption. In reactions involving the making and breaking of covalent bonds or in cases of electron-transfers which are considerably slow (Frost and Pearson),[9] this process appears to be suitable for following spectrophotometrically. The influence of $HCOO^-$ ions in deforming $I-I$ molecule or polarising it seems to be responsible for this absorption change. When such a deformation or electron-transfer is not possible, there is no increase in absorption in the ultraviolet. This is shown by a negative effect in such combinations as Acetic Acid and Iodine or Oxalic Acid and Iodine. Though there is simultaneous production of I_3^- ions in the reaction from HI and I_2 this alone does not appear to be the main cause for an increased absorption because, as will be shown later in our future publications, this kind of change is observed in many other reactions where such a possibility is avoided. The more general aspects of the discussion from the recent works of Mullikan[10] and Bruylants et al.;[11] have been given in the theoretical introduction in another paper.

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CATALYTIC ACTIVITY OF HYDRATED FERRIC OXIDE TOWARDS THE DECOMPOSITION OF HYDROGEN PEROXIDE*

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We have shown in earlier papers that the yellow hydrated ferric oxide obtained by the slow precipitation in the presence of an excess of ferric chloride, by potassium sulphate or potassium dichromate, and by the addition of smaller amount of alkali, has several characteristic properties similar to $\gamma - Fe_2O_3$ but differs in certain properties such as its inability to form ferrite with silver or copper salts. It was, therefore, thought necessary to study the catalytic activity of this yellow ferric oxide and other samples towards the decomposition of hydrogen peroxide (as has been studied by various workers on different surfaces)[1-4] and to compare the same with red variety of hydrated oxide obtained by the precipitation of an equivalent amounts of ferric chloride and caustic soda solutions. The influence of ageing of different samples on their catalytic activity has also been recorded.

EXPERIMENTAL

The following samples of hydrated ferric oxides were prepared and the composition of the interacting solutions may be represented in the table given below :—

Sample	Volume of 0·3N NaOH	Volume of 0·1M $FeCl_3$	Volume of 0·5M K_2SO_4	Volume of water
1-Y	100 c.c.	1000 c.c.	200 c.c.	700 c.c.
4-Y	400 c.c.	1000 c.c.	200 c.c.	400 c.c.
4-B	400 c.c.	1000 c.c.	200 c.c.	400 c.c.
B-E_q	1000 c.c.	1000 c.c.	—	—

All these samples after their preparation were thoroughly washed with distilled water till free from any adsorbed electrolyte, and left to age for different lengths of time.

* This paper is part VII of the series "studies in the precipitation of yellow and brown hydrated ferric oxide."

A homogeneous suspension of the precipitate was made by vigrous shaking and was analysed for its iron content by titrating 2 c.c. of the suspension solution in hydrochloric acid with potassium dichromate solution as usual using a micro-burette.

The volume of precipitate for a known value of iron (3·0 mg. atom of iron) content was calculated and taken in a conical flask and the volume made upto 50 c.c. by distilled water, 50 c.c. of a standard solution of hydrogen peroxide was taken in the reaction vessel, and the two were kept in the thermostat at temperature 31°C. After the solutions attained the temperature of the bath the two were mixed in a dark bottle and the reaction was studied at different intervals of time. 5 c.c. of the mixture of reactants was pipeted out after shaking, in beakers containing dilute sulphuric acid and large amount of ice cold water to quench the reaction. Hydrogen peroxide was titrated with standard potassium permaganate solution using a microburettee. The results are given below.

Table I

Temperature 31°C

Sample B-E$_a$ Age 24 hours

50 c.c. 0·201 N H_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture was titrated each time.

Time in minutes	Volume of 0·125N $KMnO_4$ in c.c.	K Bimolecular
1	3·25	0·0625
5	1·80	0·0681
15	0·79	0·0700
25	0·50	0·0923
35	0·29	0·1070
50	0·18	0·1090
65	0·11	0·1225
80	0·10	0·1150
95	0·09	—
∞	0·07	—

If unimolecular constant is calculated for the above readings it decreases very fast as the reaction proceeds.

Table II

Temperature 31°C

Sample B-E$_q$, Age 31 days

50 c.c. 0·207 N H$_2$O$_2$+precipitate+water=100 c.c.

5 c.c. of the mixture was titrated each time.

Time in minutes	Volume of 0·122N KMnO$_4$ in c.c.	K Unimolecular
1	4·36	0·0056 × 2·3
5	4·14	0·0055
15	3·65	0·0059
25	3·20	0·0050
35	2·75	0·0050
50	2·40	0·0052
65	2·06	0·0050
80	1·68	—
95	1·45	—
110	1·20	—
∞	0·11	—

Table III

Sample 1-Y, Age 24 hours

50 c.c. 0·201 N H$_2$O$_2$+participate+water=100 c.c.

5 c.c. of the mixture titrated each time.

Time in minutes	Volume of 0·125N KMnO$_4$ in c.c.	Time in minutes	Volume of 0·125N KMnO in c.c.
1	4·10	65	3·78
5	4·10	80	3·73
15	4·08	95	3·69
25	4·01	110	3·63
35	3·94	∞	1·05
50	3·87		

Table IV

Temperature 31°C

Sample 1-Y, Age 31 days

50 c.c. 0·207 NH_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture titrated each time.

Time in minutes	Volume of 0·122 N $KMnO_4$ in c.c.	Time in minutes	Volume of 0·122 N $KMnO_4$ in c.c.
1	4·32	65	4·12
5	4·32	80	4·05
15	4·31	95	3·88
25	4·30	110	3·90
35	4·26	∞	0·79
50	4·20		

Table V

Temperature 31°C

Sample 4-Y, Age 24 hours

50 c.c. 0·201 N H_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture titrated each time.

Time in minutes	Volume of 0·125 N $KMnO_4$ in c.c.	Time in minutes	Volume of 0·125 N $KMnO_4$ in c.c.
1	4·12	65	3·49
5	4·12	80	3·38
15	3·95	95	3·29
25	3·85	110	3·22
35	3·75	∞	0·44
50	3·59		

Table VI

Temperature 31°C

Sample 4-Y, Age 31 days

50 c.c. 2·07 N H_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture titrated each time

Time in minutes	Volume of 0·122 N $KMnO_4$ in c.c.	Time in minutes	Volume of 0·122 N $KMnO_4$ in c.c.
1	4·34	65	3·80
5	4·34	80	3·67
15	4·26	95	3·54
25	4·17	110	3·36
35	4·10	∞	3·28
50	3·95		

Table VII

Temperature 31°C

Sample 4-B, Age 24 hours

50 c.c. 0·201 N H_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture titrated each time

Time in minutes	Volume of 0·125N $KMnO_4$ in c.c.	Time in minutes	Volume of 0·125N $KMnO_4$ in c.c.
1	4·12	65	3·49
5	4·04	80	3·38
15	3·90	95	3·24
25	3·80	110	3·15
35	3·74	∞	0·26
50	3·63		

Table VIII

Temperature 31°C

Sample 4-B, Age 15 days

50 c.c. 0·20N H_2O_2+precipitate+water=100 c.c.

5 c.c. of the mixture titrated each time

Time in minutes	Volume of 0.122N $KMnO_4$ in c.c.	Time in minutes	Volume of 0·122N $KMnO_4$ in c.c.
1	4·14	50	3·66
5	4·10	65	3·55
15	4·02	80	3·43
25	3·94	95	3·29
35	3·86	∞	0·18

The results presented in the above tables may be summarised as follows :—

Red or α-hydrated ferric oxide denoted by $B-E_q$ has the highest catalytic activity which decreases with the age of the precipitate. The brown hydrated ferric oxide precipitated immediately in the presence of potassium sulphate denoted by 4-B has a smaller catalytic activity which also decreased with age, whilst the yellow modification has poor catalytic activity which is little affected by age and therefore resembles $\gamma-Fe_2O_3$ as this property is concerned. Thus the different samples may be arranged in the following order when put in decreasing order of their catalytic activity.

$$B-E_q > 4-B > 4-Y > 1-Y$$
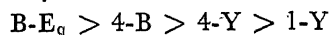
The prominence of the effect of age on their catalytic activity also follows the above order that is the sample B-E$_q$ looses its catalytic activity very soon and sample 1-Y extremely slowly. The above order is also seen for the solubility and adsorptive capacity as well.

This brings out an important fact that the catalytic activity of the hydrated ferric oxide is highly modified by the amount of alkali used in its precipitation and that the activity increases as the samples are prepared by the addition of increasing amount of alkali. Further sample 4-Y and 4-B are prepared with the same amount of alkali, still show a great difference in their catalytic activity which may be ascribed to the difference in their rate of precipitation, e.g., sample 4-B is precipitated immediately and sample 4-Y slowly.

One very interesting observation which has not been so far described by earlier workers is that the rate of decomposition of hydrogen peroxide in the presence of hydrated ferric oxide denoted by B-E$_q$ is approximately bimolecular when the precipitate is fresh and becomes strictly unimolecular after the precipitate has aged for a month (vide table II),

The rate of decomposition of hydrogen peroxide in the presence of both the brown and the yellow varieties has an auto-catalytic character. In these cases the reaction velocity constant is less than unimolecular and approaches the zero molecular order after the rate of reaction becomes steady one beyond the induction period.

It is well known that the catalytic decomposition of hydrogen peroxide in presence of Fe^{+++} ions is attended with chain mechanism involving free radicals. In view of the observations made on the heterogenous catalytic activity of hydrated ferric oxide on the reaction rate of hydrogen peroxide decomposition, we suggest the following mechanism.

On the surface of the hydrated ferric oxide the ferric ions in the crystal lattice initate the reaction.

$$Fe^{+++}+H_2O_2 \rightleftharpoons Fe^{+++}(OH)+OH \text{ (neutral)} \quad \dots\dots\dots\dots(1)$$

where iron become quadrivalent. Bray and Gorin[6] have also reported the formation of $Fe^{++}O$. The extent of the above reaction (1) will obviously depend on the adsorptive capacity of the hydrated ferric oxide and will be guided by the simple adsorption isotherm $\frac{x}{m}=KC^{\frac{1}{n}}$. Since the active area with a fresh sample of hydrated $a-Fe_2O_3$ is very large and hence the saturation on the surface is not complete and therefore reaction (1) becomes proportional to hydrogen peroxide concentration [H_2O_2]. But as this hydroxide is aged the number of area of active centres decreases so that the saturation is reached for whatsoever concentration of hydrogen peroxide. The initation of decomposition of hydrogen peroxide, affected by the generation of free radical OH is dependent on the hydrogen

peroxide concentration H_2O_2 when fresh α-hydrated ferric oxide denoted by B-Eq is used as catalyst, but becomes independent of it with the aged samples. The OH radical thus generated causes the decomposition of hydrogen peroxide by the following accepted mechanism.

$$OH + H_2O_2 = HO_2 + H_2O \qquad \dots\dots\dots\dots(2)$$
$$HO_2 + H_2O_2 = H_2O + OH + O_2 \qquad \dots\dots\dots\dots(3)$$
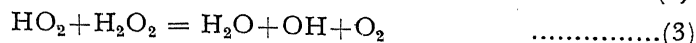
Thus a chain in the decomposition is produced (compare Haber and Weiss[7]). But the following reactions are also likely to occur as chain breaking ones.

$$Fe^{+++} + OH = Fe^{+++}(OH) \qquad \dots\dots\dots\dots(4)$$
$$OH + OH = H_2O_2 \qquad \dots\dots\dots\dots(5)$$

If we postulate that the reaction (2) is slow and (3) is fast, the rate of decomposition of hydrogen peroxide will be guided by the rate velocity of No. 2

$$-\frac{dc}{dt} = K\ [\ OH\ ]\ [\ H_2O_2\ ]$$

and as it has been already said that OH is proportional to H_2O_2 the rate of (2) will be guided by

$$-\frac{dc}{dt} = K\ [\ H_2O_2\ ]^2$$

It should be also mentioned here that the reaction (4) operating in the process of the chain breaking will be very prominent with fresh samples of hydrated α-Fe_2O_3, with the consequence that the reaction will have simplicity with a tendency to obey the bimolecular law.

As the hydrated α-Fe_2O_3 is gradually allowed to age it looses its adsorptive capacity so that, the initiation of reaction due to formation of OH becomes small and therefore the order of the chemical reaction has a tendency to decrease from a bimolecular to a unimolecular.

In one of our papers[5] we have shown that both yellow modification of hydrated ferric oxide and the brown precipitated in presence of potassium sulphate denoted by 4-B, have very low adsorptive capacity. This leads to the conclusion that the formation of OH radical from the surfaces of these hydrated oxides is initially very small with the consequence that the reaction rate is very slow. But once the reaction is initiated the reaction proceeds according to equation (2) and (3), producing OH in the chain proposed, so that the reaction takes a steady course tending to become of zero order. It is necessary to emphasise here that the chain breaking reaction (equation 4) is also not appreciable in the case of these hydrated oxides.

It will be of interest to point out here the work of Bredig (loc. cit) that the decomposition of hydrogen peroxide in presence of colloidal platinum is ordinarily bimolecular, but becomes unimolecular when the concentration of hydrogen peroxide is very low. As the adsorption on a surface is well known to be complete for the smaller concentration of adsorbate, it becomes independent of the concentration of the later. It is now easy to explain this observation from the view point that the initation of the chain by the production of OH free radical becomes independent of hydrogen peroxide concentration H_2O_3 when it is very low. This, therefore, leads the reaction of unimolecular order for lower concentration of hydrogen peroxide which becomes bimolecular when the concentration of hydrogen peroxide is increased.

Several years ago Heath and Walton[8] reported that the decomposition of hydrogen peroxide in the presence of colloidal hydrated oxide of iron is remarkably modified by the presence of the anions specially the chloride, associated with the colloidal micelle. The reaction rate velocity is decreased in presence of impurity of Cl^- ions, as the chloride ions are well known as chain breaker by the reaction.

$$OH + Cl^- \rightleftharpoons OH^- + Cl$$

It is obvious that the initation by the production of OH from the surface will be considerably lowered resulting in the decrease in the reaction rate.

Some authors have attributed the decrease in the catalytic activity of colloidal hydrated ferric oxide on ageing due to the aggregation of the colloidal units. It is true that the active surface decreases on age which can initate the chemical decomposition of hydrogen peroxide. Our results prove beyond doubt that the active surface is the main factor in this chemical reaction.

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CATALYSIS BY ORGANIC ION EXCHANGE RESINS

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The organic ion-exchange resins can be described as insoluble cross-linked polymers containing structurally bound ionogenic groups; these, for cation exchange resins in the hydrogen form may be of strongly acidic sulphonic acid type, weakly acidic carboxylic acid type and/or very weakly acidic hydroxylic type, and for anion exchange resins in the hydroxyl form may be weakly basic amino groups or strongly basic quaternary ammonium groups.

Advantages.—The cation exchange resins in the hydrogen form and the anion exchange resins in the hydroxyl form constitute new type of catalysts for a variety of reactions, known to exhibit acid-base catalysis, with unique advantages which include ease of separation of the catalyst by simple decantation or filtration, reuse of the catalyst, relative freedom from side reaction and metal contaminants and hence higher purity of the products and suitability for continuous operations.

Scope.—In addition to the fascinating possibilities of direct practical applications, catalysis by ion-exchange resins has also opened a new field of theoretical interests in that what is normally simple homogeneous catalysis, has been transformed into a heterogeneous system and comparative detailed studies may lead towards the better understanding of the mechanism of the heterogeneous reactions.

Early work.—The early work in this field was carried out in Germany[1, 2] during the last World-War and later by Sussman[3] in U. S. A. The German investigators, using Wofatit cation exchange resins, which were of phenolic type, studied reactions including esterification, ester hydrolysis and ester interchange and their efforts had enabled them to successfully operate a large scale plant for esterification. Sussman[3] made an exploratory study of a variety of reactions including esterification, ester hydrolysis, ester alcoholysis, acetal synthesis, acetal alcoholysis, alcohol dehydration and sucrose inversion. Several types of organic cation exchanges were used and their reuse was demonstrated. Of particular interest was the direct esterification of furfuryl alcohol with acetic acid, and though the yields were low, no resinification was observed, whereas usual soluble acids cause considerable resinification, rendering the direct process unsuccessful.

Reactions catalysed.—This has been followed, in the last half a dozen years or so, by the extension of this application to a variety of reactions. The cation exchange resins in the hydrogen form have been used as catalysts for sucrose inversion,[4-9] ester hydrolysis,[10-16] esterification,[17-19] halogenation of ketones,[20] preparation of *n*— and isobutyl fatty acids,[21] hydration of iso-olefins to tertiary alcohols,[22] preparation of aliphatic ethers from iso-olefins and alcohols,[23] conversion of acetaldehyde to para aldehyde,[24] vulcanization of rubber,[25] preparation of acetals,[26, 27] glucoside preparation,[28, 29] preparation of phenol from cumene,[30] hydrolysis of glycine peptides,[31] uronoside formation,[32] polymerisation reactions,[33] preparation of 2, 4, 5 tri-chloro-phrioxy acetic acid[34] and amino acid recemisation.[35]

The anion exchange resins in the hydroxyl form have been used as catalysts for mutarotation of glucose,[36] hydrolysis of nicotinonitrile to nicotinomide,[37] aldol condensation,[38-40] cyanohydrin formation,[39] benzoin condensation,[39] cyanoethylation,[39, 40] nitro-alcohol formation,[39] knoevenagel condensation[39-40] and decomposition of diazoacetic ester and nitroso alkylurea.[41]

Sucrose inversion.—The kinetics of sucrose inversion catalysed by organic cation exchange resins have been studied by Mariani[4] and by Bodamer and Kunin.[5] Mariani studied the reaction catalysed by Amberlite IR—100, a sulphonic acid resin of phenolic type at different temperatures. He observed that resin particle size influenced the rate of inversion markedly, finer mest resin giving a more rapid inversion, and concluded that the rate of diffusion of sucrose into the resin particle was an important factor in controlling the rate of inversion.

Bodamer and Kunin[5] used Amberlite IR—C50, a polymethyacrylic acid based on carboxylic acid resin and Amberlite IR—120, a polystyrene based sulphonic acid resin, of varying particle size and porosity as catalysts and· studied the inversion of sucrose at different temperatures. Their results indicated that the catalysed reaction was of first order with respect to sucrose, but the specific reaction rate appeared to decrease when the resin 'concentration' was increased. With decreasing particle size and increasing porosity the reaction rate increased, supporting the conclusion of Mariani.[4] The sulphonic acid cation exchange resin was less effective than an equivalent amount of hydrochloric acid and the energy of activation was lower than that for the homogeneous reaction. They also observed that while sulphonic acid resins caused rapid inversion, the carboxylic type resin was a relatively poor catalyst for this reaction, and hence they suggested that sucrose may be inverted, *cf.*[9] rapidly and continuously, as for the manufacture of liquid, sugar, by the passage of sucrose solutions over a bed of sulphonic acid resins at a suitable temperature, whereas carboxylic acid type resin should be useful when the removal of ionic material from sugar solutions, without the occurrence of inversion, is desired.

Ester hydrolysis.—Smith and Amundson[10] have studied the effect of intra-particle diffusion in catalytic heterogeneous systems and the relative importance on the overall rate process. The hydrolysis of ethyl formate, using a polystyrene based sulphonic acid resin, Dowex—50, of varying particle size was studied and the results obtained for both betch and continuous flow reactors, in general, validated the derived equations. Their work indicated that diffusion may be a factor in some hetrogeneous processes.

Selectivity in the hydrolysis of esters as a function of the size of the reacting molecules was studied by Duel, Solms, Anyas-Weisz and Huber[1ᵏ] and little catalytic effect of the resin was observed in the hydrolysis of high molecular weight compounds.

Mariani[11] studied the hydrolysis of ethyl acetate by a phenolic type sulphonic acid resin, Amberlite IR—100 at different temperatures in aqueous and aqueous-acetone media. He observed that in water, the hydrolysis was faster than that with an equivalent amount of hydrochloric acid. The resin, in an aqueous solution of not more than 35% acetone, was also more effective than hydrochloric acid; for larger proportions of acetone, it was less effective. The hydrolysis of ethyl acetate by anion exchange resins was studied by Mariani and Baldass,[12] who observed that hydrolysis was to a limited, nearly constant value, per gram of the anion exchange resin.

Hammett and co-workers[13, 14] have investigated the hydrolysis of several carboxylic esters in 70% acetone-water medium catalysed by cation exchange resins at different temperatures. They observed that the order with respect to the ester was one and the specific rate of the resin catalysed reaction was proportional to the 'concentration' of the resin. The catalyst was less effective than hydrochloric acid in equivalent amounts, and the reaction rate increased only slightly when the particle size was decreased. A significant specificity with respect to both, the ester and the resin was observed. An increase in the degree of cross-linking decreased the rate to different extents, for different esters. They considered that their observations were consistent with the hypothesis that the resin catalyst imposes a loss in internal entropy of the ester molecule, which accompanies its fixation on the skeleton of the resin catalyst in the formation of the transition state, its magnitude differing from ester to ester; and the effects were not dependent on the diffusion rate of the ester through the resin particle.

Thomas and Davies,[15] on the other hand, have studied the ester hydrolysis in aqueous medium by phenolic type sulphonic acid and carboxylic acid resins, Amberlite IR—100 and Wofalit C, at different temperatures. Methyl and ethyl acetates in aqueous solutions underwent hydrolysis according to the first order

rate equation, whereas with n-butyl and benzoyl acetates the reaction was of zero order, so long as ester was present as a separate phase. For equivalent amounts, the resins were more effective catalysts than hydrochloric acid, and increasing so, as the molecular weight of the ester increased. It was observed that reaction rate constant fell off towards the end of the reaction. The specific reaction rate also decreased when the concentration of the ester or the resin was increased, but it was unaffected when the ester was present as a separate phase. The effect of the variation of the particle size was slight and there was a marked drop in the apparent energy of activation as the chain length increased.

The sulphonic acid resins was a better catalyst than the carboxylic acid. From their insults, they considered that, in general, the reaction rates would be governed, not only by solubilities, but also by the relative adsorption of the reactant, product and the solvent molecules at the resin surface, and the apparent divergence between their results and those of Hammett and co-workers[13], [14] could be explained, if it was assumed that in 70% aqueous acetone the esters were negatively absorbed by the resin, and increasingly so, with increasing molecular weight, for which there appeared to be some evidence.

Esterification.—The kinetics of esterification of butanol and oleic acid were studied by Levesque and Craig[17] with a strong acid resins as catalyst. Their results indicated that the reaction was essentially second order, after an initial slow period and the velocity constant for the reaction was directly proportional to the surface area of the catalyst.

Saletan[18] has studied the esterification of acetic acid and ethanol using fixed bed of cation exchange resin in continuous flow reactors under steady state conditions. On equivalent basis, the resin was more effective as catalyst than hydrochloric acid. His results indicated that for high (diffusively/reaction rate) ratio, the reaction was proportional to resin mass, which for low ratio, it was proportional to resin surface and has suggested that the conflicting results of Levesque and Craig,[17] claiming the reaction rate to be proportional to resin surface and of Hammett and co-workers[13], [14] (and also of Thomas and Davies)[15] claiming the reaction rate to be proportional to resin mass, were understandable. For, the rate of increase of specific reaction velocity constants with temperature is, in general, considerably greater than the rate of increase of diffusivity with temperature, hence all other considerations aside, Hammett et. al. working at lower temperatures should have a higher (diffusivity/rate constant) ratio than Levesque and Craig, working at elevated temperatures; further the former workers used a low molecular weight (and hence a high diffusivity system), while the latter used a high molecular weight (low diffusivity) system. The 'induction

'period' mentioned by Levesque and Craig could be the time required by the slow moving molecules to set up diffusion gradient inside the resin.

Acetone-iodine reaction.—The reaction between acetone and iodine catalysed by a polystyrene based sulphonic acid resin is being studied by the author.[20] After a detailed consideration of the various variables involved, a method giving reproducible results was developed for following the reaction rates based on conductivity measurements and some of the results obtained are briefly summarised below :

Tables I (*a*, *b*, *c*) and Fig. 1 illustrate the reproducibility of the data and that the order of the catalysed reaction with respect to iodine is zero, as it is for the homogeneous catalysed reaction, but the zero order rate constant falls off at the latter part of the reation. $(I_2)_c$ denotes the conc. of iodine solution after resin and iodine solution had been stirred for 17 hours. The resin catalyst, 20, 30 mesh had moisture content 25·9% and capacity 3·79 m. eq./gm. air-dry resin.

Table I

Illustration of zero order law for the resin catalysed reaction between acetone and iodine.

. $10^4 (I_2)_c$, 15·25 N ; Resin (air-dried), 2 gms.

Temperature 30·1°C., Rate of stirring, 1050 r.p.m., Vol. of the solution 450 c.c.

Table I (a)

t	$10^{-3}R$	$10^4/R$
(min.)	(ohms)	(mhos)
5·0	9·10	1·099
33·3	3·60	2·778
64·5	2·26	4·425
93·3	1·76	5·682
121·8	1·49	8·711
∞	1·15	8·696

Table I (b)
(Experiment repeated)

t	$10^{-3}R$	$10^4/R$
10·2	6·75	1·481
21·7	4·60	2·174
43·1	2·97	3·367
51·8	2·59	3·861
78·6	1·95	5·128
143·0	1·37	7·299
∞	1·15	8·696

Table I (c)

(Experiment repeated, r. p. m. 450)

t	$10^{-3}R$	$10^4/R$
10·2	6·75	1·481
17·0	5·15	1·942
30·4	3·73	2·681
40·0	3·15	3·175
52·5	2·55	3·922
∞	1·15	8·696

When the concentration of acetone is increased and the zero order rate constant is plotted against the concentration of acetone, the plot is not linear which is contrary to that for the homogeneous reaction, and the slope of the plot decreases as the acetone concentration is increased. Table II and Fig. 2 illustrate the above.
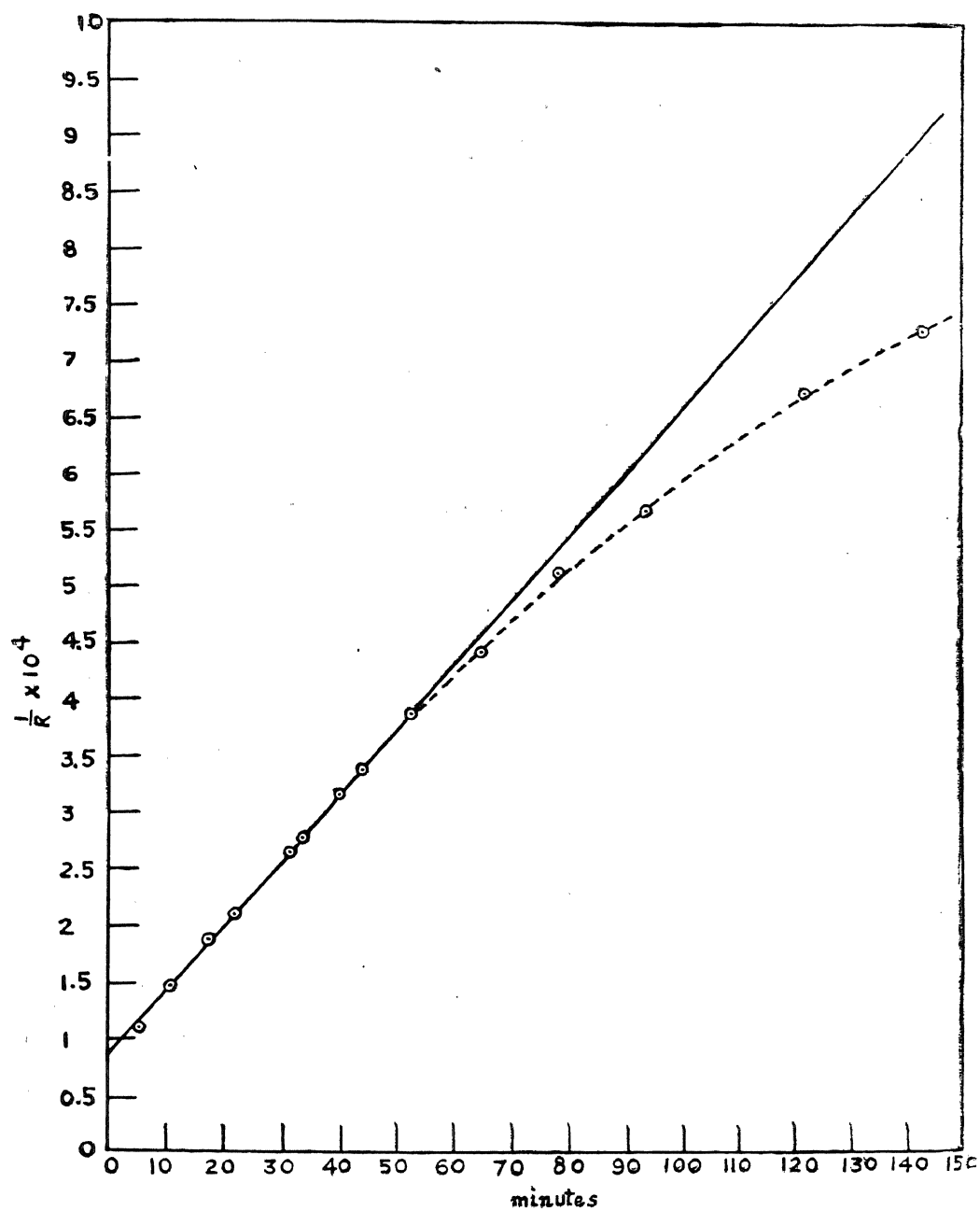
Table II

Effect of variation of acetone concentration on the reaction between acetone and iodine.

Resin (air-dried) 2 gms., temp. 30·1°C., rate of stirring 1050 r. p. m.

Volume of solution 450 c.c., t_f denotes the time for total reaction as calculated from graphs; $10^4 (I_2)_c$, 15·25N.

Acetone (c.c. in 450 c.c.)	t_f (min.)	$10^3/t_f$	$10^6 (I_2)_c/t_f$
0·25	802	1·247	1·901
0·50	420	2·381	3·631
0·75	297	2·367	5·134
1·00	234	4·274	6·516
2·00	137	7·299	11·13
3·00	99	10·10	15·40
4·00	78	12·82	19·54

When the concentration of the resin catalyst is increased, similar results are obtained as indicated by table III.
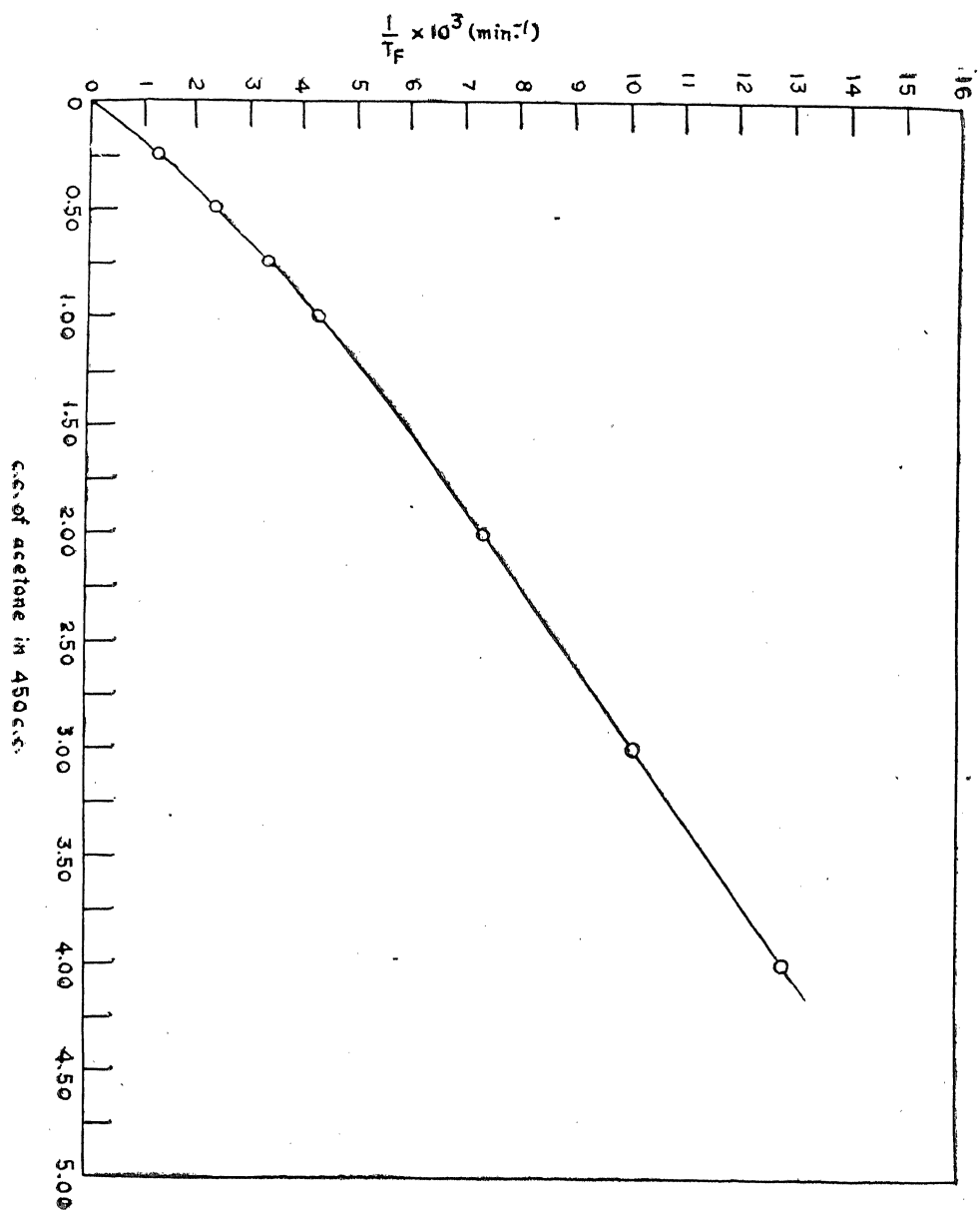
Fig I

Fig.2.

Table III

Effect of variation of resin on the reaction between acetone and iodine. Temp. 30·1°C., vol. of the solution 450 c.c., rate of stirring 1050 r. p. m.

Resin (air-dry, in gms.)	$10^4(I_2)_c$ (N)	t_f (min)	$10^6(I_2)_c/t_f$
0·50	20·61	570	3·616
0·75	20·38	390	5·226
1·00	14·95	228	6·557
2·00	15·25	137	11·13
3·00	14·95	95	15·73
4·0	14·34	67	20·40

The results also indicate that the resin catalyst is more effective than hydrochloric acid in equivalent amounts. These results compare with those obtained by Thomas and Davies[15] for ester hydrolysis.

Without going into the discussion, it may be better postponed when further results are available from the work in progress.

Conclusion.—The studies described above amply illustrate the possibilities of these new type of catalysts for both applied and fundamental work, and it is hoped that this paper may help to stimulate the interest of the workers of this country also in this new and relatively yet largely explored field.

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THE MECHANISM OF MOLECULAR ACTIVATION AND THE SPECTROSCOPIC METHOD FOR THE DETERMINATION OF THE VELOCITY CONSTANT OF THERMAL AND PHOTOCHEMICAL REACTIONS

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So far various hypotheses have been advanced to explain the mechanism of activation of molecules in thermal and photochemical reactions. The fundamental concepts on which all these hypothesis are founded, are two, *viz.*, the activation is initiated (*a*) by molecular collisions (*b*) by direct absorption of the radiations. In the photochemical reactions, it has been admitted that the reactions proceed as a result of direct absorption of the light energy, but in the thermal reactions mechanism is controversial. Perrins[1] and Dushman's[2] equations, which were based on the radiation theory could not stand the experimental tests and so the radiation theory was regarded rather superfluous. Lindemann's[3] solution of the problem of unimolecular reactions and the advancement of the theory of Absolute Reaction Rates[4] added more weight on the collision mechanism. But these theories have not been able to interpret satisfactorily the frequency factor "A" in Arrhenius equation $K = A e^{-Q/RT}$ (where symbols have their usual meanings). The general application and the verification of the absolute reaction rate theory is rather difficult owing to the factor ' σ ' the mean diameter of the activated complex which is involved in the calculations.

In the following lines I give the Radiation Theory in an entirely new form and also an equation obtained thereby, analogous to Arrhenius equation, on the basic concepts of energy transitions in molecules. The derivation of the equation and the detailed theory is under application somewhere else. The gist of the theory is given below :—

(*i*) Molecules are activated by the direct absorption of energy radiations.

(*ii*) The absorption of radiant energy changes the rotational, vibrational and electronic states of the molecules and so the activation of the molecules signify merely the changes in these energy states of the molecule.

(*iii*) A definite amount of each of the rotational, vibrational and electronic energies are required to decompose a molecule. If the required amount of any

one of these energies is not received by the molecule, the molecule will not decompose even when one type of energy supplied be tremendously great.

(iv) The radiant energy is absorbed in matter not in the form of a single indivisible quanta, but it is dissipated into simplar fragments of rotational, vibrational and electronic energies which have the nature of quantas.

In other words the mechanism of the absorption of radiations is just a reverse of the production of these radiations and the equation

$$hv = hv_r + hv_v + hv_e$$

$$\text{or} \quad v = (v_r + v_v + v_e)$$

is true in both the radiation and absorption processes (Raman Effect is the greatest support for the fact that energy of a photon can undergo a partial transformation within matter).

On the basis of these modifications in the quantum concept of radiations, the following equations have been derived for the *"Matter-Energy Equilibrium State."*

$$k = (v_r + v_v + v_e) . \ e^{-Nh \ (v_r + v_v)/RT}$$

$$\text{or} \quad k = ve^{-Nh \ (v-v_e)/RT} \qquad \qquad \dots\dots\dots\dots\dots(1)$$

$$= ve^{-Q/RT} \qquad \qquad \dots\dots\dots\dots\dots(2)$$

In equation (1) 'v' represents the frequency of the continuous absorption spectra of reaction system, and 'v_e' represents the difference between the first and second electronic levels of the spectra. Thus from the spectroscopic data, the velocity constant of any chemical reaction can be calculated by the application of equation (1). In equation (2) 'Q' represents the activation energy which is measurable from temperature coefficient of chemical reaction.

For the molecules which do not require any rotational or vibrational energies for their decomposition (*i.e.*, the molecules whose absorption spectra is situated far away from the infrared regions) the above equations reduces to the form

$$k = ve^{-Q/RT} \qquad = v$$

$$\therefore \quad hk = hv \qquad \qquad = E$$

In these special cases alone the equation $E = kv$ is applicable.

The whole crux of the problem of the validity of the Radiation Theory lies in calculating the frequency of absorption spectra from the kinetics data avail-

able for N_2O_5.   The following table of Daniels and Johnston[5] gives the velocity constants at different temperatures, and the heat of activation :

Temperature (C)	k	Heat of activation
65	0·292	
55	0·0900	25,830
45	0·0299	22,750
35	0·00808	25,370
25	0·00203	25,100
0	0·0000472	24,240

Mean 24,700 calories.

From this data the velocity constant, with the time expressed in seconds, are given by the formula[6].

$$log\ k = 31·45 - \frac{24700}{RT}$$

comparing the above equation with equation (1), we have

$$log_e\ v\ \ \ \ \ = 31·45$$

$$\text{or}\ \ log_e \left(\frac{c}{\lambda} \right) = 31·45 \qquad \text{(c is the velocity of light and λ wave length).}$$

$$\therefore\ \lambda\ \ \ \ \ \ \ \ \ \ = 62,700\ A$$

This value of 'λ' is not only of the same order but lies in the close vicinity of spectroscopically obtained value[7, 8] (58000 A).   From the nature of the equation (2) it can be noted that a slight error in the measurement of 'Q' may result considerable difference in 'v'.

Chief Characteristics of the Equation :—

(a) The equation gives the equilibria conditions of Matter—and Radiant Energy; (b) It unifies the branches of chemical kinetics, photochemistry and spectroscopy; (c) It gives the simplest and most accurate method for measuring the velocity constants of chemical reactions ; (d) It proves that the mechanism of all the thermal and photo-chemical reactions is the same.

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